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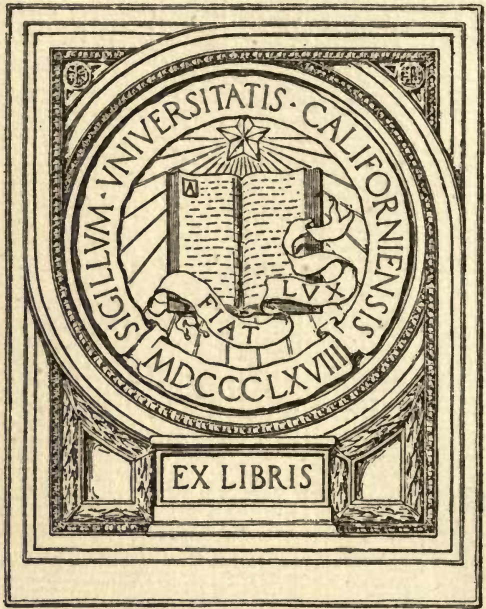
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THE THEORY OF VALENCY

THE THEORY OF VALENCY

BY

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PREFACE

It seems rather remarkable that no treatise should be extant in our own language on such an important subject as valency. Nor is the German literature in a much better position, for it contains but one monograph on the subject, written by Dr. F. Willy Hinrichsen in 1902. This, though excellent, can scarcely be regarded as exhaustive. Moreover, during the past six years much new material has been collected, and calls for rearrangement and discussion.

Perhaps this lack of systematic treatment of the subject is to be ascribed to the difficulty of reconciling any theory of valency with the facts of inorganic chemistry. But the remarkable success which has attended our application of the theory to the study of organic chemistry may be regarded as a guarantee that we are on the right track, and should serve to stimulate us, rather than otherwise, in our attempts to perfect our theory. It has been my endeavour in the present volume to present to the reader a concise account of the more important theories of chemical combination, which have exercised the minds of scientific men down to the present day.

The determination of the numerical value of the valencies of the elements is not always easy. The Periodic Classification, however, frequently gives us help in this direction, and has therefore received full treatment in the text. Some of my readers may be surprised that Dulong and Petit's Law of Specific Heats has not been discussed. The answer is, that, if the atomic weights of the elements are deduced by the help of this law, their valencies can be determined by reference to the Periodic Table. Further, it must be borne in mind that the law is at best only an approximation to the truth, and that it usually fails, as in the case of glucinum, just when we require its assistance most. Finally, it is desirable in any series of text-books to avoid overlapping, and, for a full treatment of our knowledge of the specific heats of the elements, the reader is referred to the volume on "The Relation between Chemical Constitution and Physical Properties," by Dr. Samuel Smiles (this Series).

A complete treatise on the theory of valency might also be expected to include a thorough study of stereoisomerism. But this branch of chemistry has been extended within recent years to such an enormous degree, that whole books are devoted to its treatment alone. I have, therefore, contented myself with referring to the subject in just sufficient detail to give an idea of the supposed configuration of certain atoms, and the directions in which their valencies are believed to act. For further details the reader is recommended to consult Dr. Stewart's volume entitled "Stereochemistry" (this Series).

The elements have been studied in the order in which they occur in the Periodic Table, with the single exception of carbon, whose importance seemed to justify its inclusion in a separate chapter earlier in the work.

The nomenclature adopted is substantially the same as that used by the Chemical Society (London), and I would here gratefully acknowledge the kind assistance rendered to me by Dr. J. C. Cain, who carefully read through the proof-sheets with a view to checking the nomenclature. It will be observed that I have uniformly employed the Greek prefixes, mono-, di-, tri-, etc., although the formation of such hybrids as monovalent, monomolecular, etc., is the inevitable result. It seems to me that more is gained by securing uniformity in prefixes, than is lost by the introduction of a few additional hybrids.

As my readers will have observed, the words *valency* and *valence* are used synonymously by many writers. I have found it advantageous to distinguish between the two terms. Whilst the former is given its usual meaning, namely, the power possessed by atoms generally to combine with one another, the latter is defined as the actual force or bond effecting that union. Thus, hydrogen may be said to possess a single valence, because its valency is unity.

It is hoped that the numerous references in the text will be of assistance to the student, by putting him in touch with the more important papers dealing with the subjects under discussion. The abbreviations are practically identical with those used by the Chemical Society. I believe that all sources from which information has been derived are duly acknowledged in the text, with the single exception of Meyer's "Geschichte der Chemie," which was used freely in the preparation of Chapter II.

To Sir William Ramsay my best thanks are due for reading through this work in manuscript, and for making several useful suggestions. I would also tender my very heartiest thanks to Mr. William Turner, M.Sc., who has not only assisted in the correction of the proof-sheets, but has checked the majority of the references to original papers.

J. N. F.

November, 1908.

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THE THEORY OF VALENCY

I

LAVOISIER, DALTON, AND BERZELIUS

INCREASE in knowledge necessitates change of ideas. The old theories which were suggested by the ancients to account for the phenomena of nature have been gradually discarded as their insufficiency became realized, and out of their ruins have sprung up the various hypotheses, theories, and laws, which engage our attention to-day. Thus it was that the theory of valency was not suddenly sprung upon chemists without any warning. It was the natural result of gradual growth.

In order to trace its history, therefore, we have to go back to the time of Lavoisier (1743–1794). To this eminent chemist belongs the honour of having struck the death-blow to the theory of phlogiston, which lay at the base of all the chemical thought and speculation of his day. It was Lavoisier who, following the example of Black, urged upon chemists the necessity of using the balance, and of studying chemical problems not merely qualitatively, but quantitatively also.

The Laws of Combustion which he established may be cited as follows:—[1]

1. Bodies burn only in pure air.
2. The air is used up during combustion, and the increase in weight of the combustible substance is equal to the loss in weight of the air.
3. Combustible bodies are usually converted into acids by combining with the air. Metals, on the other hand, yield metal calces (*basic oxides*).

---

[1] Oeuvres II. 226. "*Mémoire sur la combustion en général.*"

In these laws we see the first step towards a theory of definite chemical composition. The way was being paved for the reception of new ideas, so soon to be introduced by John Dalton (1766–1844).

In 1808, the whole world of chemical thought was revolutionized by the appearance of a book entitled *A New System of Chemical Philosophy*, from the pen of John Dalton. In it, the author propounded the famous Atomic Theory,[1] with which his name is inseparably associated.

Not that Dalton was the first to propose an Atomic Theory of matter. No one has ever seriously urged this on his behalf. That matter was composed of minute, indivisible masses had been long maintained by the philosophers of Rome and Greece. Democritus,[2] some 2300 years before Dalton, had suggested the atomic hypothesis as opposed to the alternative suggestion that matter could be divided up indefinitely.

Dalton's great merit lay in explaining the facts of chemical combination by means of atoms.

His theory may be stated concisely as follows :—

1. Every element is composed of homogeneous atoms, whose weight is constant.
2. Chemical compounds are formed by the union of atoms of different elements in the simplest numerical proportions.

In order to indicate the composition of chemical substances,

---

[1] The way in which Dalton was led to the conception of his atomic theory does not concern us here. Until quite recently it was believed that he first discovered the Law of Multiple Proportions, and that the atomic theory was the outcome of an attempt to explain it. In 1896, however, Roscoe and Harden published a pamphlet entitled *A New View of the Origin of Dalton's Atomic Theory*, in which evidence is adduced to show that such was not the case. It appears that the theory existed in Dalton's mind as a preconceived notion, and that experiment was resorted to in order to verify it. A very clear statement of the whole case is given by J. P. Millington in his book entitled *John Dalton*, 1906, Chapters VII. and VIII. See also *Avogadro and Dalton*, by A. N. Meldrum, 1904.

[2] An interesting discussion as to the originator of the theory of atoms appeared in *Nature*, 1908, February 13, p. 345 ; February 20, p. 368 ; March 26, p. 486 ; and April 9, p. 541. See also Freund, *The Study of Chemical Composition*, 1904, Chapter IX.

Dalton introduced a system of nomenclature. Thus we find written in his laboratory notebook the following entry, dated September 6th, 1803:—

"CHARACTERS OF ELEMENTS.

○ Hydrogen.
⊙ Oxygen.
⦶ Azote.
● Carbone, pure charcoal.
⊕ Sulphur."

The composition of compounds was therefore written as follows:—

Water	○⊙
Ammonia	⦶○
Nitrous oxide	⦶○⦶
Carbonic acid	⊙●⊙

and so on.

It is interesting to note that a few years later, Dalton, accidentally or otherwise, interchanged the symbols for oxygen and hydrogen, thus:

Oxygen	○
Hydrogen	⊙

Fortunately, about this time, namely in 1811, Berzelius[1] introduced another system of chemical nomenclature, which prevented the cumbersome invention of Dalton from coming into general use. This consisted in using the first letter or letters of the name of the element—sometimes the modern, and sometimes the Latin. A small number placed below the letter indicated the number of atoms of that element present in a molecule of the compound. Thus water was expressed by the formula H_2O, and marsh gas by CH_2.

Curiously enough Dalton[2] could never be brought to realize that the symbols of Berzelius were far more simple than his own. Writing to Graham in 1837, he says—

---

[1] Berzelius, *Journ. de Physique*, **73**, 257.

[2] See *John Dalton and the Rise of Modern Chemistry*, Roscoe, 1895, p. 148.

> "Berzelius's symbols are horrifying: a young student in chemistry might as soon learn Hebrew as make himself acquainted with them. They appear like a chaos of atoms . . . and to equally perplex the adepts of science, to discourage the learner, as well as to cloud the beauty and simplicity of the Atomic Theory."

But Dalton stood alone. No chemist was blind to the disadvantages of his cumbersome system. Every one realized that the great founder of the Atomic Theory had assumed an untenable position. The fact that the Berzelian system of nomenclature is at the present time in general use, forms no small tribute to its simplicity, and to the genius of its inventor.

Were Dalton alive to-day, and confronted with the task of representing the composition of bodies like indigo and the alums by his unwieldy method, there can be no doubt that he, too, would be led to acknowledge the superiority of the Berzelian system.

II

EARLY THEORIES OF CHEMICAL COMBINATION

It seems at first sight very remarkable that chemists were not led to a conception of valency by the enunciation of Dalton's Law of Multiple Proportions, supported as this was by Wollaston's[1] substitution of empirically determined *equivalents* for Dalton's hypothetical atomic weights. Although it was now known that compounds were formed by the union of atoms of different elements in varying proportions, the idea that the individual atoms possessed a definite attractive force was seemingly never entertained.

After Nicholson and Carlisle had, on May 2nd, 1800, performed their famous experiment of the decomposition of water by the electric current, the close connection between chemical affinity and electrical force began to be realized. This was made still more evident by the experiments of Henry, who effected the decomposition of nitric and sulphuric acids by similar means. Three years later, namely in 1803, Berzelius and Hisinger discovered that, by means of the voltaic current, the elements of water, and the acids and bases of neutral salts, could be separated. In 1805, Brugnatelli observed the electric deposition of gold upon silver, when the former was made the negative pole in a solution of "ammoniuret of gold." Finally Sir Humphry Davy, on October 6th, 1807, effected the electrolytic decomposition of potash and soda, with the liberation of their respective metals, by a current from a battery of 274 cells.

Ritter, in his work entitled *Elektrisches System*, adduced evidence to show that electricity results from chemical decomposition, and as this is the necessary complement of electrolysis, it is clear that the way was being paved for the formation of an electro-chemical theory of chemical combination.

---

[1] Wollaston, *Phil. Trans. Roy. Soc.*, 1814, **104**, 1.

Davy[1] proposed one such. It was characterized by the supposition that the small particles of substances, which have an affinity for one another, become oppositely electrified only upon contact.

In 1812, Berzelius[2] enunciated his famous Dualistic Theory. Volta had arranged the metals according to the electric tension which he had found them to exhibit after contact with each other. Those metals which admit of easy oxidation constituted the positive end of the series, and those with a small affinity for oxygen, the negative end. This faculty of exciting each other electrically was not confined by Berzelius to the metals, but was attributed to all the other elements to a greater or less degree. At the extreme positive end of the series were placed the newly discovered alkali metals. At the negative end oxygen and the halogens found a place. Each atom was assumed to possess two poles of opposite sign, but the amount of electricity was not the same on each. Hence the element derived its character from the stronger pole. This explains very readily many simple reactions, such, for example, as those involved in the oxidation of the metals. In the case of copper we have

EARLY VALENCY

$$\overset{+}{\mathrm{Cu}} + \overset{-}{\mathrm{O}} = \mathrm{CuO}.$$

Since copper oxide possesses basic properties, it was assumed that the positive charge on the copper exceeded the negative charge on the oxygen, so that the resulting copper oxide is slightly charged with an excess of positive electricity. A similar explanation served to account for the negative charge on the group SO_3, for it was attributed to the excess of negative electricity supplied by the three oxygen atoms over that required to neutralize the positive possessed by the sulphur. It was therefore to be expected that copper oxide and sulphur tri-oxide would combine to form a very stable salt. Thus:

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[1] Davy, *Phil. Trans.*, 1807, p. 1; see also Chapter XIX.

[2] Berzelius, *Schweigger's Journ.*, 6, 119. His *Versuch über die Theorie der chemischen Proportionen und über die chemischen Wirkungen der Elektricität* appeared first in 1814 in Swedish, in 1819 in French, and in 1820 in German (Dresden).

$$\overset{+}{\mathrm{CuO}} + \overset{-}{\mathrm{SO}_3} = \mathrm{CuSO}_4.$$

Berzelius frequently drew attention to the fact that certain elements exhibit positive polarity with regard to some atoms, and negative polarity with regard to others. For example, in its oxides, sulphur is positive to oxygen, but in its hydride it is negative to hydrogen. Oxygen, however, was regarded as a typically negative element, for it was not known to act positively to any other element. But the strictly dualistic view cannot be reconciled with the fact that hydrogen and oxygen combine to yield water. Thus:

$$2\mathrm{H}_2 + \mathrm{O}_2 = 2\mathrm{H}_2\mathrm{O}.$$

Since the compound natures of the hydrogen and oxygen molecules could only be due to the fact that the constituent atoms possessed different charges, it is difficult to see how the two resulting molecules of water can be identical in every respect. Yet experiment shows that such is the case. Further, Faraday proved that the same quantity of electricity passing through an electrolyte always sets free, or transfers to other combinations, the same number of units of affinity at both electrodes. Thus, for each atom of oxygen set free at the positive electrode, two atoms of hydrogen are formed at the negative, or one atom of copper (from a cupric salt). In other words, the quantity of electricity required is independent of the degree of affinity—a fact which is fatal to the Berzelian theory. Finally, Daniell pointed out that, when copper sulphate is electrolyzed, it is split up into $\mathrm{Cu}(+)$ and $\mathrm{SO}_4(-)$ ions, and not into $\mathrm{CuO}(+)$ and $\mathrm{SO}_3(-)$ as the dualistic theory would lead us to expect.[1]

We may now pass on to consider the application of the

---

[1] See Lehfeldt's *Electrochemistry* (this series), p. 26 *et seq.*

Berzelian theory to organic chemistry, which was then in its infancy.

Wöhler's remarkable synthesis of urea from ammonium cyanate showed that two compounds could exist having the same chemical composition, and yet possessed of totally distinct properties.[1] Other examples were speedily discovered. Berzelius[2] himself proved that racemic acid has the same composition as tartaric acid. To explain this, he assumed that the atoms were arranged differently in the two compounds, or *isomers*, as he termed them. Not that he had conceived a spatial arrangement such as that which has led to the construction of that vast branch of science known to-day as stereochemistry. Berzelius regarded the composition of these bodies from the point of view of radicles, and, together with Liebig, he was led in this way to play an important part in the development of the Older Theory of Radicles.

The origin of the theory of radicles lay in the discovery that cyanogen, besides being known in the free state, acted like a single element when combined with other groups. It was thought that other radicles might therefore exist, and that organic bodies owed their properties to the possession of these. Wöhler and Liebig's[3] classical research on the radicle of benzoic acid lent strong support to this view. These investigators proved that a radicle, which they termed *benzoyl*, and to which the formula $C_{14}H_{10}O_2$ was assigned, was present in benzoic acid, benzoyl chloride and bromide, benzamide, benzoic ether, and benzoyl sulphide.

Berzelius, as we have already remarked, was a strong supporter of this radicle theory, in so far as it did not interfere with his dualistic notions. He insisted on the necessity of assuming a binary structure for all organic bodies, just as for inorganic.[1] He denied, however, the possibility of oxygen being a constituent of a radicle, for this element was regarded by him as electro-negative, and incapable of functioning in any other capacity.[2] Benzoyl was explained as the oxide of the complex $C_{14}H_{10}$, the peroxide of this being anhydrous benzoic acid.

---

[1] This was not the first case of isomerism to be discovered. Some five years previously, namely in 1823, Liebig drew attention to the fact that silver fulminate and silver cyanate possess the same qualitative and quantitative composition. The above example of urea and ammonium cyanate is quoted, however, on account of its being best known.

[2] Berzelius, *Jahresber.*, 1832, **11**, 44.

[3] Wöhler and Liebig, *Annalen*, 1832, **3**, 249; see also *ibid.*, 1838, **25**, 1; Ostwald's *Klassiker*, Nr. 22.

Whilst Berzelius was inclined to the opinion that radicles were unalterable, Liebig's[3] views were broader. In 1838, he mentioned three characteristics by which a radicle may be distinguished :

1. It is the unchanging constituent of a series of compounds.
2. It can be replaced by simple substances.
3. When combined with a single element the latter can be exchanged for its equivalent of another element.

These views gave an enormous impetus to the study of organic chemistry. The famous researches of Bunsen[4] on the cacodyl compounds, begun in 1839, were a direct outcome of them, and have since been classed with the work of Gay Lussac on cyanogen, and of Wöhler and Liebig on the benzoyl radicle, as the pillars of the radicle theory.

In 1834, Dumas,[5] after a study of the reactions involved in the production of chloral from alcohol, drew up two empirical Laws of Substitution. These may be expressed as follows :—

1. When a compound containing hydrogen is exposed to the action of chlorine, bromine, or iodine, it takes up an equal volume of the halogen for each atom of hydrogen displaced.
2. If the compound contains water, it loses the hydrogen of this without displacement.

Laurent[6] went a step further and suggested what is known as the Substitution Theory, which hinged on the doctrine that the structure and chemical character of organic compounds are not materially altered by the entrance of chlorine and the separation of hydrogen.

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[1] Berzelius, *Jahresber.*, 1833, **13**, 190.

[2] It is true that, for a short time immediately succeeding the discovery by Wöhler and Liebig of the benzoyl radicle, Berzelius discarded his idea that oxygen could not be a constituent of a radicle. But he reverted to his old assumption again soon after.

[3] Liebig, *Annalen*, 1838, **25**, 3.

[4] Bunsen, *Ann. Chem. Pharm.*, **31**, 175 ; **37**, 1 ; **42**, 14 ; **46**, 1.

[5] Dumas, *Ann. Chim. Phys.*, 1834, (2) **56**, 113 and 140.

[6] Laurent, *Ann. Chim. Phys.*, (2), **60**, 223 ; **61**, 125 ; **66**, 326.

Although Dumas warmly opposed these views he was led to suggest his Theory of Types,[1] which in some respects resembled the substitution theory of Laurent. According to Dumas—

Every chemical compound forms a complete whole. Its chemical nature depends primarily on the arrangement and number of the constituent atoms, and to a lesser degree on their chemical nature.

This was in direct opposition to the Berzelian dualistic theory. As might be expected, Berzelius defended himself vigorously, but his theory was incompatible with the discoveries of Dumas, and chemists were compelled to abandon it. He, alone, stood by it to the last.

In 1839, Gerhardt[2] propounded his Theory of Residues. By residues he understood atomic complexes which remain over from the interaction of two compounds, as the result of the stronger affinity of certain elements for one another, and which combine together because they cannot exist separately. His views, however, were considerably modified by the researches of Wurtz,[3] and Hofmann,[4] on the organic ammonium compounds, and of Williamson[5] and Chancel[6] on the ethers.

In 1856, Gerhardt[7] enunciated his new Theory of Types. By means of this theory he was able to arrange organic compounds according to four types, namely, ammonia, water, hydrogen, and hydrochloric acid.

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[1] Dumas, *Ann. Chim. Phys.*, **33**, 179 and 259.

[2] Gerhardt, *Ann. Chim. Phys.*, 1839, (2) **72**, 184.

[3] Wurtz, *Compt. rend.*, 1849, **28**, 223 ; *Ann. Chim. Phys.*, (3) **30**, 498.

[4] Hofmann, *Annalen*, 1850, **74**, 174.

[5] Williamson, *Annalen*, 1851, **77**, 33 ; **81**, 73.

[6] Chancel, *Compt. rend.*, **31**, 521.

[7] Gerhardt, *Ann. Chim. Phys.*, 1856, (3) **37**, 331. *Traité de Chimie*, 1856, iv. 568.

The following examples will serve to illustrate the classification :—

1. The Ammonia type.

$$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N \qquad \left.\begin{matrix}CH_3\\H\\H\end{matrix}\right\}N \qquad \left.\begin{matrix}C_2H_3O\\H\\H\end{matrix}\right\}N \qquad \left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}P$$

Ammonia. Methylamine. Acetamide. Tri-ethyl phosphine.

2. The Water type.

$$\left.\begin{matrix}H\\H\end{matrix}\right\}O \qquad \left.\begin{matrix}CH_3\\H\end{matrix}\right\}O \qquad \left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O \qquad \left.\begin{matrix}C_2H_3\\H\end{matrix}\right\}O$$

Water. Methyl alcohol. Acetic anhydride. Aldehyde.

3. The Hydrogen type.

$$\left.\begin{matrix}H\\H\end{matrix}\right\} \qquad \left.\begin{matrix}CH_3\\H\end{matrix}\right\} \qquad \left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\}$$

4. The Hydrochloric acid type.

$$\left.\begin{matrix}H\\Cl\end{matrix}\right\} \qquad \left.\begin{matrix}CH_5\\Cl\end{matrix}\right\} \qquad \left.\begin{matrix}C_2H_5\\CN\end{matrix}\right\}$$

These views underwent alteration at the hands of Williamson and others, who assumed the existence of mixed types. Thus, benzenesulphonic acid was written as:

$$\begin{array}{l}\left.C_6H_5\right\}\\ \left.\begin{matrix}SO_2\\H\end{matrix}\right\}O\end{array} \quad \text{referred to} \quad \begin{array}{l}\left.\begin{matrix}H\\H\end{matrix}\right\}\\ \left.\begin{matrix}H\\H\end{matrix}\right\}O\end{array}$$

and carbamic acid as :

$$\begin{array}{l}\left.\begin{matrix}H\\H\end{matrix}\right\}N\\ \left.\begin{matrix}CO\\H\end{matrix}\right\}O\end{array} \quad \text{referred to} \quad \begin{array}{l}\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\\ \left.\begin{matrix}H\\H\end{matrix}\right\}O\end{array}$$

Kekulé,[1] in 1857, introduced a fifth type, namely that of marsh gas, and illustrated it by the following examples :—

$$\left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\}C_2 \qquad \left.\begin{matrix}H\\H\\H\\Cl\end{matrix}\right\}C_2 \qquad \left.\begin{matrix}H\\Cl\\Cl\\Cl\end{matrix}\right\}C_2 \qquad \left.\begin{matrix}H\\H\\H\\CN\end{matrix}\right\}C_2$$

Marsh gas. Methyl chloride. Chloroform. Acetonitrile.

[1] Kekulé, *Annalen*, 1857, **101**, 200. See *Kekulé Mem. Lecture*, Japp, 1897.

In Gerhardt's theory of types we see the germ of a theory of valency. In a paper communicated to the *Chemical Gazette* in 1851, and afterwards reprinted in full in the *Transactions of the Chemical Society*,[1] Williamson pointed out that certain compound radicles, like NO_2, can replace one atom of hydrogen in a molecule of water, and thus give rise to a monobasic acid, thus—

$$H.OH \longrightarrow NO_2.OH,$$

whilst others, like SO_2, can replace two atoms of hydrogen in two molecules of water, yielding a dibasic acid, thus—

$$\begin{array}{l} H.OH \\ H.OH \end{array} \longrightarrow SO_2\begin{array}{l} .OH \\ .OH \end{array}$$

From this it is clear that Williamson realized that radicles or groups possess a definite attractive or expulsive force.

Since the fall of the dualistic theory of Berzelius, chemists had given but little attention to the older theory of radicles. Kolbe now revived this idea, and stripping it of all the untenable assumptions with which Berzelius had clothed it, he was able to put new life into it. The main result of Kolbe's theorizing may be expressed in the following terms:—

> "Organic compounds are all derivatives of inorganic, and result from the latter by exceedingly simple substitution processes."

Thus,[2] the alcohols, ketones, aldehydes, and carboxylic acids were derived from carbonic acid, $(C_2O_2)O_2$, and its hydrate, $C_2O_2\begin{array}{l} OHO \\ OHO \end{array}$.

It is interesting in this connection to note the views advanced by Crum Brown,[3] in 1861, which take an intermediate position between Gerhardt's theory of types, and Frankland's theory of valency. The author points out that all the four types of Gerhardt may be brought under that of hydrogen, $n\genfrac{}{}{0pt}{}{H}{H}$, where n is a whole number. The molecule of hydrogen may be regarded as composed of two atoms connected together by a single line of force, thus :

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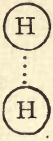
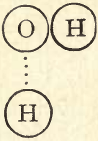
[1] Williamson, *Trans. Chem. Soc.*, 1852, **4**, 350.

[2] See Kolbe, *Annalen*, **113**, 293.

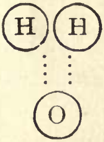
[3] Crum Brown, *On the Theory of Chemical Combination*, 1861, first published in March, 1879, Edinburgh.



A molecule of water belongs either to the single or double hydrogen type according as we write it as



or



where *n* equals 1 and 2 respectively. Similarly ammonia, NH_3, may be regarded as belonging to the single, double, or treble hydrogen type, thus :

$$\left\{\begin{matrix}NH_2\\H\end{matrix}\right. \qquad \left\{\begin{matrix}NH\\H_2\end{matrix}\right. \qquad \left\{\begin{matrix}N\\H_3\end{matrix}\right.$$

where *n* equals 1, 2, and 3 respectively. It will be observed that the numerical value of *n* is the same as that of the number of lines of force joining the atoms together. In those schemes where *n* is a maximum its value is given by half the sum of the valencies of the atoms composing the molecule. It is easy to see that by extending these views, even complex organic bodies may be represented according to the simple or multiple hydrogen type. Thus in ethyl alcohol,[1] C_2H_6O, *n* is equal to 8, and the molecule may be represented by the scheme $8\genfrac{}{}{0pt}{}{H}{H}$.

Although these different theories contained an element of truth, they were yet wide of the mark. It was reserved for Frankland to clear away the majority of these misconceptions by giving expression to a definite theory of *atomic* attractive force, now known as *valency*. In the next chapter we shall show how he was led to conceive such a brilliant idea.

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[1] See also Crum Brown, *Trans. Chem. Soc.*, 1865, **18**, 230 ; *Proc. Roy. Soc. Edin.*, 1866, **5**, pp. 429 and 561.

III

THE THEORY OF VALENCY

WE have already seen in the preceding chapter that it was reserved for Frankland to add the finishing touches to the theories of chemical combination, by giving expression to the idea of a definite atomic attractive force, now known as valency.

In 1852, Frankland published his classical paper in the *Philosophical Transactions*,[1] entitled *A New Series of Organic Compounds containing Metals.* In this a detailed account was given of his researches on the organic derivatives of arsenic, antimony, zinc, tin, and mercury. Frankland then proceeded to show that individual atoms, as distinct from groups, possess a definite power of entering into chemical combination.

Since this observation is one of such fundamental importance, Frankland's own words may be quoted :—

> "When the formulæ of inorganic chemical compounds are considered, even the superficial observer is struck with the general symmetry of their constitution ; the compounds of nitrogen, phosphorus, antimony, and arsenic especially exhibit the tendency of these elements to form compounds containing 3 or 5 equivalents of other elements, and it is in these proportions that their affinities are best satisfied ; thus in the ternal group we have NO_3, NH_3, NI_3, NS_3, PO_3, PH_3, PCl_3, SbO_3, SbH_3, $SbCl_3$, AsO_3, AsH_3, $AsCl_3$, etc. ; and in the five-atom group NO_5, NH_4O, NH_4I, PO_5, PH_4I, etc. Without offering any hypothesis regarding the cause of this symmetrical grouping of atoms, it is sufficiently evident, from the examples just given, that such a tendency or law prevails, and that, no matter what the character of the uniting atoms may be, the combining power of the attracting element, if I may be

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[1] See also *Annalen*, 1853, **85**, 329.

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allowed the term, is always satisfied by the same number of these atoms."

That these ideas of Frankland were only slowly accepted by chemists is shown by Odling's[1] paper *On the Constitution of Acids and Salts.* The observations recorded are explained according to the Theory of Types. Odling argued that salts and acids, especially such as contain oxygen, may be referred to the simple or multiple water type, in such a way that the hydrogen of the latter is partially or completely substituted by elementary or compound radicles of definite replaceable value. Again, in the publications of Wurtz[2] and Gerhardt,[3] the saturation capacity of the nitrogen atom was discussed, although Frankland had given expression to similar views some three years previously. No doubt an explanation for this may be found in the fact that Frankland had employed Gmelin's equivalents, a procedure which did not impress the adherents of the type theory with the value of his work, to the extent to which it might otherwise have done.

In 1858 two papers appeared simultaneously, by Couper[4] and Kekulé,[5] in which Frankland's views were enlarged, and the theory of valency was placed on a firm foundation. Couper rejected the type theory entirely, and constructed formulæ for various compounds by applying his knowledge of the valencies of the constituent atoms. Had he employed the same atomic weights as we do to-day, namely, $C = 12$ and $O = 16$, his formulæ would in many cases have been the same as are still in vogue. He had, however, peculiar views of his own. Whilst the atomic weight of carbon was regarded as 12, that of oxygen was taken as 8. Carbon was a tetrad, and oxygen a diad. Since, however, the atoms of the latter were supposed to be always linked in pairs, thus O....O, this group was diadic, and was therefore practically identical with our present conception of the atom O = 16. As illustrative of his system, the following formulæ may be given :—

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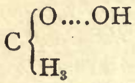
[1] Odling, *Trans. Chem. Soc.*, 1854, **7**, 1.

[2] Wurtz, *Ann. Chim. Phys.*, 1855, (3) **43**, 492.

[3] Gerhardt, *Traité de Chimie*, 1856, iv. 595 and 602.

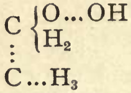
[4] Couper, *Ann. Chim. Phys.*, 1858, (3), **53**, 469; *Compt. rend.*, 1858, **46**, 1157; English transl., *Phil. Mag.*, 1858, (4) **16**, 104.

[5] Kekulé, *Annalen*, 1858, **106**, 129.



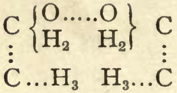
$$C\left\{\begin{matrix}O\ldots.OH\\ \\ H_3\end{matrix}\right.$$

Methyl alcohol.



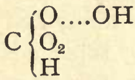
$$\begin{matrix}C\left\{\begin{matrix}O\ldots OH\\ H_2\end{matrix}\right.\\ \vdots\\ C\ldots H_3\end{matrix}$$

Ethyl alcohol.



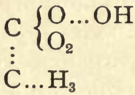
$$\begin{matrix}C\left\{\begin{matrix}O\ldots\ldots O\\ H_2\quad H_2\end{matrix}\right\}C\\ \vdots\qquad\qquad\qquad\vdots\\ C\ldots H_3\quad H_3\ldots C\end{matrix}$$

Ethyl ether.



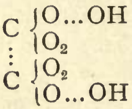
$$C\left\{\begin{matrix}O\ldots.OH\\ O_2\\ H\end{matrix}\right.$$

Formic acid.



$$\begin{matrix}C\left\{\begin{matrix}O\ldots OH\\ O_2\end{matrix}\right.\\ \vdots\\ C\ldots H_3\end{matrix}$$

Acetic acid.



$$\begin{matrix}C\left\{\begin{matrix}O\ldots OH\\ O_2\end{matrix}\right.\\ \vdots\\ C\left\{\begin{matrix}O_2\\ O\ldots OH\end{matrix}\right.\end{matrix}$$

Oxalic acid.

Kekulé, on the other hand, was impregnated with the type theory, and endeavoured to harmonize the new views with the old. The fact that he so early recognized the value of the theory of valency is not to be attributed to any care with which he studied Frankland's epoch-making paper, but rather to the fact that he had independently been led to somewhat similar conclusions. In fact, Kekulé regarded *himself* as the founder of the theory, as is evident from his statements in a paper on the atomicity of the elements.[1] Nevertheless, the first occasion on which he referred to valency was in a paper on Thiacetic acid, published in 1854, some two years after the appearance of Frankland's paper. Further, in the introduction to his *Lehrbuch*, Kekulé made no mention of Frankland, although the work of Williamson, Odling, Hofmann, and Wurtz received full recognition. This was no doubt due to the fact that Kekulé regarded valency as a constant property, and a theory of variable valency, as upheld by Frankland, was to him no theory of valency at all.

Variability of Valency

The early development of the theory of valency was beset with difficulties. It is true that hydrogen formed an excellent standard, in that its atom was never known to combine with more than one atom of any other element. The numerical value of its valency was therefore to be taken as unity, and by analyzing its hydrides, the valency of any other element might be determined.

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[1] Kekulé, *Compt. rend.*, 1864, **58**, 510.

But not only was this method unsatisfactory on account of the paucity and instability of the metallic hydrides known, it also yielded contradictory results. Thus, writing the formula for hydrochloric acid as $H . Cl$, it is clear that the valency of chlorine can only be unity. Now two chlorides of phosphorus are known, namely the trichloride, PCl_3, and pentachloride, PCl_5, in which the valency of phosphorus is three and five respectively. It is obvious, therefore, that if the above reasoning is valid, valency cannot be regarded as a constant quantity. Both Frankland and Kolbe were of this opinion.

Kekulé,[1] on the other hand, preferred to regard valency as a fundamental property of the atom, and as unchangeable and invariable as the atomic weight. This view he retained to the last. In order to explain the formation of phosphorus pentachloride, Kekulé argued that its formula would be more correctly written as $PCl_3 . Cl_2$. The fact that this substance dissociates on vaporization was taken as supporting his view. A similar explanation was applied in the case of ammonium chloride, to which the formula $H_3N . HCl$, was given, since the nitrogen was regarded as trivalent. During the past few years, however, a large number of facts has been accumulated, which cannot be reconciled with Kekulé's doctrine of constant valency, and to these we shall have occasion to refer in succeeding chapters.

Kolbe[2] believed that each element possessed a definite maximum valency, and that, when this was saturated, further combination became impossible. Erlenmeyer,[3] some years later, adopted a similar view. Mendeléeff[4] assumed that the highest oxygen compounds, omitting peroxides, give the maximum valency of the elements, and Abegg[5] has adopted the same suggestion.

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[1] Kekulé, *Zeit. Chem.*, **7**, 689.

[2] Kolbe, *Lehrbuch d. anorg. Chem.*, 1856, Vol. I.

[3] Erlenmeyer, *Zeit. Chem.*, 1863, pp. 65, 97, and 609; 1864, pp. 1, 72, and 628.

[4] Mendeléeff, Ostwald's *Klassiker*, **68**, 48.

[5] Abegg, *Zeit. anorg. Chem.*, 1904, **39**, 340.

But not only is this method uncertain owing to the divalent nature of oxygen, it is also inconsistent. The valency of manganese, for example, is decided by a much higher and more unstable oxide, namely the heptoxide, Mn_2O_7, than the peroxide, MnO_2, as Friend[1] has already pointed out. Abegg[2] further suggests that the maximum valency of every element is eight, and apparently Morozoff[3] is of the same opinion. Although this is true for the majority of the amphoteric[4] elements, it is difficult to realize that this is so for the inert gases, hydrogen, and the alkali metals—to mention extreme cases.

Up to the present, no satisfactory theory has been advanced to account for the variability of valency. Abegg assumes that all the valencies of an atom are of the same strength before actual combination, but saturation of one weakens the rest. The extent of that weakening determines the numerical value of the valency in the circumstances.

Nef, on the other hand, believes that the unused valencies do not lie latent in the ordinary sense of the term. They saturate one another. He therefore writes $Cl \equiv Cl$ for the molecule of chlorine, whose atom he regards as trivalent, $R{-}Cl>$ for alkylchlorides, and $H_3N>$ for ammonia.[5]

This theory, however, offers no explanation for the existence of but *one* unsaturated valence, such as occurs in bromine and iodine at high temperatures, the molecules of which are then monatomic.[6] Similarly in nitric oxide, N : O, the molecule of which has been proved to be single at temperatures as low as −100° C., we have one unsaturated nitrogen valence. In the case of ferrous chloride, $FeCl_2$, and cuprous chloride, CuCl, the difficulty was overcome by doubling the formulæ, a procedure which was supported by the results of vapour density determinations.

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[1] Friend, *Trans. Chem. Soc.*, 1908, **93**, 262.

[2] Abegg, *Opus cit.*

[3] Morozoff, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, (2) 481.

[4] Friend, *Opus cit.*

[5] Nef, *Annalen*, 1897, **298**, 202.

[6] See Horstmann, *Ber.*, 1869, **2**, 137; V. Meyer, *Ber.*, 1880, **13**, 394; V. Meyer and Zublin, *ibid.*, pp. 399 and 405; Crafts, *Compt. rend.*, 1880, **90**, 183; Crafts and Meier, *Compt. rend.*, 1881, **92**, 39; Biltz and V. Meyer, *Ber.*, 1889, **22**, 725; Perman and Atkinson, *Proc. Roy. Soc.*, 1900, **66**, 10.

As we shall see later, however, the correctness of representing these substances by double formulæ has recently been called into question. It appears now, that the iron in ferrous salts is truly divalent, and copper in cuprous salts truly monovalent.

Van't Hoff [1] suggests that the phenomena of variable valency may be referred to the effect of the shape or form of the atoms. Thus, any deviation from the spherical shape must result in greater manifestations of the attractive force in certain directions, since the atom may be regarded as more accessible in these places. If an atom moves regularly in all directions about a fixed position, a change of external form must occur. This involves a change of affinity, and of valency. All the other atoms will be constrained to remain at a greater distance from the one under consideration, and consequently they will be held to it by a lesser force. In other words, the affinity of the atom is weakened.

It is easy to see that, if the motion of the atom is very greatly increased, chemical combination may become impossible, in other words, the molecule is monatomic. Now, rise of temperature is supposed to cause an increased vibratory motion amongst the atoms. We might, therefore, expect that, as the temperature is raised, the numerical value of the valency of an element would decrease. This is very frequently found to be the case.

As early as 1869, Blomstrand [2] pointed out that those elements, which are decidedly electropositive or electronegative, have the lowest saturation capacity. For example, if the halogens act decidedly negatively, their valency is always unity. Hinrichsen [3] has generalized this observation as follows :—

The energy content of an atom is inversely proportional to the degree of its affinity.

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[1] Van't Hoff, *Ansichten über die organische Chemie*, 1881, pp. 3 *et seq.*

[2] Blomstrand, *Chemie der Jetztzeit*, 1869, pp. 217 and 243.

[3] Hinrichsen, *Zeit. phys. Chem.*, 1902, **39**, 305.

Hinrichsen therefore argues that valency is truly variable. It does not lie latent in the sense in which Nef speaks of it. He agrees with Nef,[1] Gattermann,[2] Scholl,[3] and others, in regarding carbon as truly divalent in hydrocyanic acid, $C = NH$, isonitriles, $C = NR$, and fulminic acid $C = NOH$.

Several other theories have been advanced to account for the variability of valency, and will be discussed in succeeding chapters.[4]

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[1] Nef, *Annalen*, **270**, 286.

[2] Gattermann, *Ber.*, 1898, **31**, 1149.

[3] Scholl, *Ber.*, 1890, **23**, 3506 ; 1899, **32**, 3492.

[4] See Chapters XIX and XX.

p131.

IV

VALENCY AND THE PERIODIC LAW[1]

TRUE knowledge does not consist in the mere accumulation of facts. It is the power to absorb and apply these facts which marks the educated man, and distinguishes him from the mere mechanical compiler. Consequently it is not surprising that chemists and physicists alike should have endeavoured to discover some relation between those apparently isolated and sharply defined portions of matter known as elements. The very fact that we employ to-day such terms as The Halogens, The Alkali Metals, etc., indicates the innate tendency to classify things which show points of resemblance, and to distinguish things which differ.

As early as 1829 Doebereiner[2] pointed out that there are certain triads of elements which not only show remarkable resemblance in their physical properties, but also striking regularities in their atomic weights.

Pettenkofer[3] and Dumas[4] continued the study of such triads. It was found that they could be divided into two classes, namely those the atomic weights of which show approximately equal differences, and those of which the atomic weights are nearly the same. To the former group belong the elements in the adjoining table.

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[1] For more complete references to the Periodic Law the reader is referred to *The Development of the Periodic Law*, by F. P. Venable, 1896, and *The Periodic Classification and the Problem of Chemical Evolution*, by G. Rudorf, 1900. See also K. Seubert, *Zeit. anorg. Chem.*, 1895, **9**, 334.

[2] Doebereiner, *Pogg. Ann.*, 1829, **15**, 301.

[3] Pettenkofer, *Annalen*, 1858, **105**, 187.

[4] Dumas, *Compt. rend.*, 1857, **45**, 709; 1858, **46**, 951.

CLASS I.

Element.	Atomic weight.	Difference.	Mean of extreme atomic weights	Valency.
Lithium	7·03	16·02	23·09	1
Sodium	23·05	16·10		1
Potassium	39·15			1
Calcium	40·1	47·5	88·75	2
Strontium	87·6	49·8		2
Barium	137·4			2
Sulphur	32·06	47·1	79·83	2 and 6
Selenium	79·2	48·4		2 and 6
Tellurium	127·6			2 and 6
Chlorine	35·45	44·51	81·21	1
Bromine	79·96	47·01		1
Iodine	126·97			1

It will be observed that the atomic weight of the middle element of each triad is almost exactly the mean of the atomic weights of the other two. Further, the different elements in each triad exhibit the same valency.

The second group of triads is shown by the following table :—

CLASS II.

Element.	Atomic weight.
Iron	55·9
Nickel	58·7
Cobalt	59·0
Ruthenium	101·7
Rhodium	103·0
Palladium	106·5
Osmium	191
Iridium	193·0
Platinum	194·8

But the mere grouping of certain elements into triads, whilst interesting, did not yield any very fruitful results. In 1863, however, Newlands[1] introduced his famous generalization, known as **The Law of Octaves.** In a series of short articles, he drew attention to the fact that, if the elements are arranged in the order of increasing atomic weights,[2] certain periodic relations between the physical and chemical properties of the elements become apparent.

At first Newlands' papers were ridiculed and the remarkable coincidences, which they pointed out, were ascribed to chance. In 1866, at a meeting of the Chemical Society, when a paper entitled "The Law of Octaves and the Causes of Numerical Relations among the Atomic Weights" was being discussed, a critic enquired if Mr. Newlands had ever examined the elements according to their initial letters, and suggested that such a study might prove very profitable.

Newlands, however, did not pursue the subject further. If this was due to the opposition he had encountered, he certainly made a great mistake. Believing, as he did, that his views were sound and contained germs of a new truth, it was his duty as well as his privilege to see that they received both a fair hearing and a due share of consideration from men competent to judge. Pioneers in every walk of life are sure to meet with opposition. Victories are seldom won before the fight.

It was not long before Lothar Meyer and Mendeléeff realized the importance of Newlands' discovery. The former, in a series of short papers, developed the subject along lines very similar to those independently worked out by Mendeléeff. It is to both authors, therefore, that the honour of developing the Periodic Law is due.[3]

In the Table on page 24, the elements are arranged in the order of increasing atomic weights. The scheme is

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[1] Newlands, *Chem. News*, 1863–1866, *vols.* **7–13.**

[2] Although in his earlier papers Newlands wrote *equivalent weights*, he actually employed *atomic weights* throughout.

[3] Ostwald's *Klassiker der exakten Wissenschaften*, *No.* 68, contains a collection of papers by the two men.

THE PERIODIC TABLE.

O.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.		
He 4	H? Li 7·03	Gl 9·1	B 11·0	C 12·00	N 14·01	O 16·00	H? F 19·0			
Ne 20	Na 23·05	Mg 24·36	Al 27·1	Si 28·4	P 31·0	S 32·06	Cl 35·45			
A 39·9	K 39·15	Ca 40·1	Sc 44·1	Ti 48·1	V 51·2	Cr 52·1	Mn 55·0	Fe 55·9	Co 59·0	Ni 58·7
...	Cu 63·6	Zn 65·7	Ga 70	Ge 72·5	As 75	Se 79·2	Br 79·96			
Kr 81·8	Rb 85·4	Sr 87·6	Y 89	Zr 90·6	Nb 94	Mo 96	?	Ru 101·7	Rh 103·0	Pd 106
...	Ag 107·93	Cd 112·4	In 114	Sn 119·0	Sb 120·2	Te 127·6	I 126·85			
X 128	Cs 133	Ba 137·4	La 138·9	Ce 140	...	...	...	...	...	...
...	...	...	...	...	...	...	...			
...	...	...	Yb 173	...	Ta 183	W 184	...	Os 191	Ir 193·0	Pt 194·8
...	Au 197·2	Hg 200·0	Tl 204·1	Pb 206·9	Bi 208·5	...	...			
...	...	...	...	Th 232·5	...	U 238·5	...	...	...	...
Oxides Hydrides	R_2O —	RO —	R_2O_3 —	R_2O_4 RH_4	R_2O_5 RH_3	RO_3 RH_2	R_2O_7 RH	RO_4 —		

substantially the same as that drawn up by Lothar Meyer and Mendeléeff, the only important alteration being the inclusion of the inert gases in column O by Ramsay. These gases were of course unknown forty years ago.

The chief regularity which concerns us here is that of the valency exhibited by the elements in the several groups. Considering the oxygen compounds only, it will be observed that the valencies of the elements show a regular increase from 0 to 8 as we pass from group O to group VIII. On the other hand, the most stable hydrides known are formed from elements in groups IV, V, VI, and VII, which now exhibit a valency falling from 4 in group IV to 1 in group VII. From the above it is clear that if we can but determine the atomic weight of an element, the Periodic Classification will give us a valuable clue to its valency.

This was the case with

Glucinum

formerly known as beryllium. Its chloride was supposed to have the formula $GlCl_3$ and its oxide Gl_2O_3, for Berzelius regarded glucinum as trivalent owing to its resemblance to aluminium.[1] The atomic weight deduced from analyses of the compounds was accordingly 13·8. But this places the element between carbon ($C = 12{\cdot}00$) and nitrogen ($N = 14{\cdot}01$) in the Periodic Classification, and there is no room for it. If, however, we assume that the oxide has the formula GlO and the chloride $GlCl_2$, the atomic weight of glucinum is reduced to 9·1, which places it between lithium and boron. Here we have a vacancy. Moreover, the other elements in the second group show great similarity to glucinum in their chemical properties.

When, however, the specific heat was determined and divided by 6·4—the atomic heat constant—14 was obtained as the approximate atomic weight. Either, therefore, glucinum must be regarded as an exception to the Periodic Law, or to the Law of Dulong and Petit. If to the latter, then we should expect its specific heat to increase with rise of temperature, as was found to be the case with carbon, boron, and silicon. By reasoning in this way Nilson and Pettersson[1] were led to determine the specific heat of the metal at temperatures higher than 100°. They found that it increased rapidly with rise of temperature from 0·42 between 0° and 100° to 0·50 between 0° and 300°.

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[1] Berzelius, Schweigger's *Journ. Chem. Pharm.*, 17, 296.

Humpidge[2] immediately after determined the specific heat at temperatures ranging from 0° to 500°. As will be evident from the following table,[3] the atomic heat of glucinum approaches nearer and nearer to 6·4, as the temperature is raised.

Temperature.	Specific heat.	Atomic heat = Specific heat × 9·1.
0°	0·3756	3·42
100°	0·4702	4·28
200°	0·5420	4·93
300°	0·5910	5·38
400°	0·6172	5·61
500°	0·6206	5·65

It is clear, therefore, that the atomic weight of glucinum is 9·1 and that the numerial value of its valency is two.

Nilson and Pettersson[4] confirmed the divalent nature of glucinum when they determined the vapour density of its chloride, $GlCl_2$.

VAPOUR DENSITY OF GLUCINUM CHLORIDE.

Temperature.	Density.	Temperature.	Density.
490°	6·700	812°	2·793
520°	4·174	1080°	2·684
589°	3·067	1115°	2·779
686°	2·853	1184°	2·824
745°	2·753	1502°	2·791

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[1] Nilson and Pettersson, *Ber.*, 1880, **13**, 1451; 1884, **17**, 987.

[2] Humpidge, *Proc. Roy. Soc.*, 1885, **38**, 188; **39**, 4.

[3] This table is taken from *The Study of Chemical Composition*, by Freund, 1904, p. 369.

[4] *Nilson Memorial Lecture*, by Pettersson, 1900, p. 1285.

As will be seen from the above table, at temperatures ranging from 730° upwards, glucinum chloride has almost exactly the constant density 2·77 as calculated for the molecule $GlCl_2$.

Combes[1] proved in a similar manner that glucinum is divalent in the acetylacetonate, to which he gives the formula $Gl(C_5H_7O_2)_2$.

Tanatar,[2] however, holds to the opinion that glucinum is tetravalent, and that the basic acetate should be represented by the formula

$$(OC_2H_3O)_3Gl\,.\,O\,.\,Gl(OC_2H_3O)_3$$

but Boris Glasmann[3] dissents from this view.

Pollok[4] has expressed his belief that ordinary glucinum contains a small quantity of a second element of high atomic weight, but Parsons[5] objects to this assumption on the ground of insufficient evidence.

For the present, therefore, glucinum must be regarded as a divalent element, an exception to Dulong and Petit's Law,[6] but not an exception to the Periodic Law.

THE POSITION OF HYDROGEN.

For many years there has been much uncertainty as to the position of hydrogen in the Periodic Table. By general consent the valency of this element has been taken as unity, for in all binary compounds containing this element, the number of hydrogen atoms in a molecule is never less than that of the atoms of the second element, save in two cases. Thus, for example, we have the very stable hydrides of the non-metals, H_2O, H_2S, PH_3, NH_3, SiH_4, CH_4, etc., and the less stable metallic hydrides, NaH, CaH_2, etc. The two exceptions mentioned above are hydrazoic acid, HN_3, and palladium hydride, Pd_2H. In the former case we have good reason to believe that the nitrogen atoms are arranged in a ring, and that the hydrogen is attached to but one of them, thus:

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[1] Combes, *Compt. rend.*, 1894, **119**, 1222.

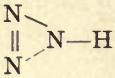
[2] Tanatar, *J. Russ. Phys. Chem. Soc.*, 1904, **36**, 82; 1906, **38**, 850; 1907, **39**, 936.

[3] Glasmann, *Chem. Zeit.*, 1907, **31**, 8; *Ber.*, 1907, **40**, 3059; see Steinmetz, *Zeit. anorg. Chem.*, 1907, **54**, 217.

[4] Pollok, *Trans. Chem. Soc.*, 1904, **85**, 1630.

[5] Parsons, *J. Amer. Chem. Soc.*, 1905, **27**, 233.

[6] Other examples of the application of this law to determine atomic weight and valency are dealt with fully by Dr. Smiles in his work entitled *The Relation between Chemical Constitution and Physical Properties* (this series).



The latter case is discussed fully in Chapter XVII. Now there are two groups in the Periodic Table, namely the first and the seventh, which contain monovalent elements, and the question is, to which group does the hydrogen belong? Mendeléeff placed hydrogen at the head of the first group, just before lithium. In favour of this position the following arguments may be urged:—

1. The most stable compounds of hydrogen, as of the metals, are those which are formed by union with non-metallic elements. Thus, for example, whilst the halogens combine but feebly amongst themselves, with the exception perhaps of the two extreme elements, iodine and fluorine, yet with hydrogen exceedingly stable compounds are formed. Admitting that combination might occur between the halogens and hydrogen, if the latter were placed at the head of group seven, just before fluorine, we should certainly expect the hydride of the more distant element, iodine, to be stabler than that of fluorine. But, as every chemist is aware, the reverse is actually the case. Consequently it seems impossible to class hydrogen amongst the halogens.

2. When acids and metallic salts are electrolyzed, both hydrogen and the metals are liberated at the cathode, whereas the non-metals migrate to the anode.

On the other hand, Orme Masson[1] and others place hydrogen at the head of the seventh group, and support their action by the following arguments:—

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[1] Masson, *Chem. News*, 1896, 73, 283.

1. Hydrogen and the halogens, when in the vaporous condition, consist of diatomic molecules. The alkali metals, however, are exclusively monatomic.

2. The melting and boiling points of the alkali metals rise as the atomic weight diminishes, as is evident from the following table:—

Metal.	Atomic weight.	Melting point.	Boiling point.
Lithium	7·03	180·0°	Red heat
Sodium	23·05	95·6°	742°
Potassium	39·15	62·5°	667°
Rubidium	85·4	38·5°	—
Caesium	133	26·5°	270°

The reverse is true for the halogens:

Halogen.	Atomic weight.	Melting point.	Boiling point.
Fluorine	19·0	—	− 185°
Chlorine	35·45	− 102°	− 33·6°
Bromine	79·96	− 7°	+ 59°
Iodine	126·85	+ 107°	+ 175°

Hydrogen, therefore, with a boiling point of −252·5°, is a more fitting forerunner of fluorine than of lithium.

3. Solid hydrogen bears no resemblance whatever to the alkali metals. It is a white solid mass, melting at −259° to a clear colourless liquid, resembling water, and having all the properties of a non-metallic element.

4. The difference between the atomic weights of any two consecutive elements in the first two horizontal series in the periodic table is practically 2·5. By placing hydrogen in the seventh group, the passage from this to helium in group O is in harmony with this regularity. If, however, hydrogen is put at the head of the first group, we must either assume that the table is discontinuous, or that a series of six new elements remains to be discovered, with atomic weights lying between

1·008 (the atomic weight of hydrogen) and 4 (the atomic weight of helium).

We thus see that there are excellent arguments in favour of including hydrogen in both the first and the seventh groups, and at present it is impossible to say which position is the more correct.[1]

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[1] See Brauner, *Chem. News*, 1901, **84**, 233.

V

EXCEPTIONS TO THE PERIODIC LAW

ALTHOUGH among the rare elements we find a few apparent exceptions to the Periodic Law, as, for example, neodymium and praseodymium, it is unnecessary for us to dwell upon them here. It is advisable to wait until their elementary nature has been demonstrated with certainty, and their physical constants determined with greater accuracy. There are, however, three well-established exceptions to the law, and these call for treatment here.

I. Argon and Potassium

On the discovery of the so-called inert gases,[1] it was necessary to introduce an entirely new group into the Periodic System, namely that to which the ordinal O has been assigned. It is obvious that by this arrangement we have greatly added to the completeness and symmetry of the system, for the inert gases form an ideal mean between the monovalent electronegative halogens and electropositive alkali metals. Reference to the table on page 24 shows that the atomic weights of helium, neon, krypton, and xenon fit into this arrangement extremely well. But the case of argon is exceptional. With an atomic weight of 39·9 the natural position of this element would lie between potassium (39·15) and calcium (40·1), where, however, there is no room. In order to account for this anomaly many explanations have been suggested.

(*a*) Some chemists have been led to dispute the elementary nature of argon. Rayleigh[1] argues, however, that both the density of argon and the ratio of its specific heats, for which the value 1·659 has been found, point conclusively to the fact that argon is not a compound.

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[1] Ramsay, *Ber.*, 1898, **31**, 3111.

(*b*) It has been suggested that argon may be a mixture of two or more monatomic gases. There are several ways by which the truth, or otherwise, of this assumption can be demonstrated.

Argon was first liquefied by Olszewski of Cracow in 1895. There was no appearance of liquid before the boiling point was reached, nor was there any alteration of temperature when the liquid argon was allowed to boil away. This is precisely what we should expect if the gas were a single substance. If, on the other hand, it were a mixture, the temperatures of liquefaction and boiling would almost certainly be indefinite.

Sir William Crookes and others have studied the spectrum of argon, and obtained some very interesting results. The spectrum consists of a large number of lines extending into the ultraviolet region. On altering the intensity of the electric discharge through the gas under low pressure by the interposition of a Leyden jar between the secondary terminals of the induction coil and introducing a spark gap, the colour of the light in the tube changes from red to blue. This, however, is no proof that the gas is a mixture.

A convenient method of separating the constituents of a gaseous mixture lies in shaking up the latter with some liquid, whereby the more soluble portions are dissolved out. Rayleigh has shown, however, that the spectrum of argon which has been thoroughly shaken up with water is identical with that of argon not so treated. We are therefore forced to the conclusion that argon is a single substance, and not a mixture.

(*c*) A third and very plausible way of accounting for the high atomic weight of argon lies in the supposition that the gas is a mixture of many monatomic and comparatively few diatomic molecules. As Ramsay[2] has pointed out, if there were only 500 diatomic molecules of the gas to every 10,000 monatomic molecules, the density would be 19, and the calculated atomic weight would be accordingly reduced to 38. This value would give argon its right position in the Periodic System.

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[1] Rayleigh, *Nature*, **52**, 159.

[2] Ramsay, *The Gases of the Atmosphere*, 1902, p. 229.

A delicate method of testing this supposition lies in the determination of γ, the ratio of the specific heats at constant pressure and constant volume. The most trustworthy result is

$$\gamma = 1{\cdot}659$$

instead of the theoretical value 1·667. A mixture of five per cent. diatomic molecules should, however, have yielded a result, $\gamma = 1{\cdot}648$. The evidence, therefore, is inconclusive.

From theoretical considerations, involving somewhat arbitrary assumptions, Thomsen[1] concludes that the atomic weight of argon may be only about 36. But speculations such as these are of little value unless they are borne out by experiment, and until further research has been done on the subject, we must be content to regard argon as an exception to the Periodic Law.

II. Cobalt and Nickel

Judging by its chemical properties we should certainly expect cobalt to lie between iron and nickel in the eighth group of the Periodic Table.

Thus, iron forms two classes of salts, namely, ferrous and ferric, in which it functions respectively as a divalent and trivalent element. Cobalt exhibits a similar tendency, but to a less extent. The cobaltic salts are unstable, and exist only in solution. Very stable double salts are known, however, as for example, potassium cobaltic nitrite, to which the formula, $K_6Co_2(NO_2)_{12} \cdot 3H_2O$, may be ascribed.[2] Nickel, on the other hand, only forms *one* series of salts, namely, the nickelous, in which it functions as a divalent atom. Further, by placing cobalt between iron and nickel, the resemblances between the elements in the vertical columns of the eighth group are better brought out. Thus, iron, ruthenium and osmium form compounds of the type $K_4M(CN)_6$; cobalt, rhodium and iridium form $K_3M(CN)_6$; and the elements of the last column, namely, nickel, palladium and platinum, yield double salts corresponding to the formula $K_2M(CN)_4$.

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[1] Thomsen, *Zeit. anorg. Chem.*, 1895, 9, 283.

[2] Rây, *Trans. Chem. Soc.*, 1906, 89, 551.

But the atomic weight of nickel, as determined in a variety of ways by a number of careful investigators, is always found to be slightly less than that of cobalt. Krüss and Schmidt[1] thought that this was due to the presence of a hitherto undiscovered element, to which they gave the name *gnomium.* Winkler,[2] however, has shown that this explanation is very improbable.

During the past few years, Richards, Baxter, and others have been determining the atomic weights of nickel and cobalt afresh, but as yet the difficulty has not met with solution.

III. Tellurium and Iodine

A glance at the accompanying table will show that tellurium very closely resembles selenium and sulphur in its chemical properties.

ANALOGOUS COMPOUNDS OF

Tellurium.	Selenium.	Sulphur.
TeO_2	SeO_2	SO_2
TeO_3	SeO_3	SO_3
TeH_2	SeH_2	SH_2
$TeCl_4$	$SeCl_4$	SCl_4
TeF_6	SeF_6	SF_6.
$TeAg_2$	$SeAg_2$	SAg_2

This analogy is still further illustrated by the discovery of Pellini,[3] that the hydrogen rubidium salts of selenic and telluric acids are isomorphous. It should be mentioned, however, that Staudenmaier[1] several years ago made the interesting observation that potassium tellurate is not isomorphous with the corresponding sulphate, but with potassium osmate. There can be no reasonable doubt, therefore, that the true position of tellurium in the Periodic Classification lies in the sixth group, and not in the seventh with manganese and the halogens.[2] Nevertheless, the atomic weight of tellurium, as determined by a large number of reliable workers in a variety of ways, is almost invariably found to be approximately 127·6, which is slightly *greater* than that usually accepted for iodine, namely 126·97.

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[1] Krüss and Schmidt, *Ber.*, 1889, **22**, 11 and 2026.

[2] Winkler, *Ber.*, 1889, **22**, 890; *Zeit. anorg Chem.*, **4**, 10.

[3] Pellini, *Atti R. Accad. Lincei.*, 1906, (v.) **15**, i. 629 and 711; ii. 46.

Whether this is due to experimental error in the determination of the atomic weights of the two elements, or to the fact that we have here a real exception to the Periodic Law, is difficult to say. Scott,[3] from a consideration of the differences in the atomic weights of the elements in the sixth group, concludes that the atomic weight of tellurium should be above that of iodine. Brauner,[4] who studied the subject for many years, gave expression to the view that tellurium is a mixture of two elements, which cannot be separated by chemical means. In support of this he pointed out that the more carefully the tellurium is purified, the lower does the atomic weight apparently become. Thus, for example, if the tellurium is first distilled in hydrogen before the tetrabromide is prepared and analyzed, the atomic weight thus found is appreciably lower than if the metal is merely fused in a current of inert gas before the same treatment.

One might, perhaps, imagine that the recent investigation of Baker and Bennett[5] would settle, for this generation at any rate, the vexed question as to whether tellurium is a mixture or not. But as we shall see presently, no research is final, and we must be prepared to alter our views, even on the most trivial subjects, should the necessity for so doing arise. The element with which Baker and Bennett experimented was obtained from Bohemian tellurium, West Australian ores, South American ores, and finally from a specimen prepared by Divers from Japanese sulphur deposits. The crude substance was dissolved in aqua regia and evaporated several times with hydrochloric acid. The gold, bismuth, lead, thallium, silver and selenium were removed by treatment with sulphur dioxide. Fusion with alkali cyanides in a current of coal gas and subsequent treatment with water and air yielded needle-shaped crystals of tellurium. The element was purified by alternate oxidation and reduction, and finally by distillation in a current of pure hydrogen. The authors now sought to determine if the tellurium could be separated into two or more elements, and to this end employed the following methods:—

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[1] Staudenmaier, *Zeit. anorg. Chem.*, 1895, **10**, 189. See Muthmann, *Zeit. Krystall.*, **17**, 336. See Retgers, *Zeit. phys. Chem.*, 1891, **8**, 6.

[2] Compare Gutbier and Flury, *J. pr. Chem.*, 1907 (ii.) **75**, 99.

[3] Scott. *Proc. Chem. Soc.*, 1902, **18**, 12.

[4] Brauner, *Trans. Chem. Soc.*, 1889, **55**, 382. Brauner is not now of this opinion, however; see *Trans. Chem. Soc.*, 1895, **67**, 549.

[5] Baker and Bennett, *Trans. Chem. Soc.*, 1907, **91**, 1849.

1. Telluric acid, obtained by oxidation of the element, was fractionally crystallized, and each fraction subjected to separate analysis. If two acids were really present, one would expect them to show a slight difference in solubility. The several fractions should, therefore, possess different oxygen contents. The ratio $TeO_2 : O_2$ was, therefore, determined, but was found to be constant. Further, Sir William Crookes examined the extreme fractions spectroscopically, and proved their absolute identity.

2. The second method was based on the assumption that if two acids were present in telluric acid, the difference in the solubilities of their barium salts would offer a means of separation. Analysis of the different portions, however, gave identical results.

3. Tellurium was fractionally distilled.

4. Tellurium dioxide and tetrachloride were each fractionally distilled.

5. Tellurium was converted into hydride and fractionally decomposed.

6. Tellurium tetrachloride and tetrabromide were submitted to fractional electrolysis.

7. Tellurium tetrachloride was fractionally precipitated by water.

In no case, however, could any difference in the atomic weight of tellurium be observed. The mean of forty-three determinations gave 127·605 ($O = 16$) as the atomic weight. These results are in good agreement with those obtained by Lenher.[1] The recent work of Marckwald,[2] however, must not be omitted. This investigator examined about 1500 grams of hydrated telluric acid, $H_2TeO_4 . 2H_2O$, and, after several hundred crystallizations, obtained twenty fractions of approximately equal weight. No difference could be observed between the extreme fractions. A lower value than that of Baker and Bennett was obtained for the atomic weight of tellurium, namely 126·85—a number which places the element in its proper position in the Periodic Table. This result, however, cannot be accepted as final. It must not be forgotten that Baker and Bennett also analyzed the hydrated telluric acid, but obtained inconstant results, the variation in 26 determinations being from 126·8 to 128·2. This they attribute to inconstancy in the amount of water of crystallization.[3] Marckwald only performed six experiments, and it has yet to be proved that the constancy of his results was not due to coincidence. Further, if this lower number is accepted, an explanation will have to be given for the higher values repeatedly obtained by every other method.

Bettel,[4] in a very interesting communication to the *Chemical News*, has raised the vexed question again as to the possibility of tellurium being a mixture of two elements. Observing in 1883 that some silver obtained from assays of a silver telluride ore behaved in an unusual manner at the apparent completion of cupellation, Bettel endeavoured to determine the cause. The results of his experiments, performed in order to determine if a new element were present, were inconclusive, and by giving publicity to the fact he hopes to draw the attention of scientific and commercial men to this unsolved problem. Baker, however, does not believe that the phenomenon described by Bettel is caused by the presence of a new element in tellurium.

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[1] Victor Lenher, *J. Amer. Chem. Soc.*, 1908, **30**, 741.

[2] Marckwald, *Ber.*, 1907, **40**, 4730.

[3] Baker, *Chem. News*, 1908, **97**, 209.

[4] Bettel, *Chem. News*, 1908, **97**, 169.

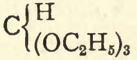
The last twenty years, therefore, do not seem to have brought us a single stage nearer to the solution of the difficulty, and for the present tellurium must be regarded as an exception to the Periodic Law.

VI

THE VALENCY OF CARBON

THE determination of the numerical value of the valency of carbon was an important advance in the theory of valency, and one destined to exert an enormous influence on the study and progress of organic chemistry.

In 1854, Williamson and Kay[1] prepared tri-ethyl orthoformate,



$$C\left\{\begin{matrix}H\\(OC_2H_5)_3\end{matrix}\right.$$

by the action of chloroform on sodium ethoxide. Thus:

$$CHCl_3 + 3NaOC_2H_5 = 3NaCl + CH(OC_2H_5)_3$$

They described it as "a body in which the hydrogen of three atoms of alcohol is replaced by the tribasic radical of chloroform."

It is most remarkable that the study of this body did not lead them to the discovery of the tetravalency of carbon. This honour was seemingly reserved for Kekulé. In a paper on the constitution of fulminic acid, Kekulé[2] drew up a table of the compounds belonging to the marsh-gas type. Thus:

"C_2	H	H	H	H	Marsh gas.
C_2	H	H	H	Cl	Methylic chloride.
C_2	H	Cl	Cl	Cl	Chloroform.
C_2	(NO_4)	Cl	Cl	Cl	Chloropicrin.
C_2	H	H	H	(C_2N)	Acetonitrile.
C_2	(NO_4)	Hg	Hg	(C_2N)	Mercuric fulminate."

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[1] Williamson and Kay, *Proc. Roy. Soc.*, 7, 135.

[2] Kekulé, *Annalen*, 1857, **101**, 200.

It is clear from this table that Kekulé regarded C_2 as tetravalent, where by C_2 he understood Ȼ, the symbol used by the Gerhardt-Williamson school to denote the atom $C = 12$. In a paper published later[1] in the same year, Kekulé distinctly states in a footnote that he regards one atom of carbon, Ȼ $= 12$, as equivalent to four atoms of hydrogen.

Both Kolbe[2] and Frankland[3] claimed to have anticipated Kekulé in his discovery of the tetravalency of carbon, and in support of their statements drew attention to a paper published by themselves in 1857.[4] As this appeared so soon after the first one of Kekulé, there can be no doubt that these authors had arrived independently at the conclusions contained therein. The tetravalency of carbon is certainly implied in the paper, but is nowhere expressly stated, and it is very doubtful if the authors realized its significance at the time. A second paper by Kekulé, which appeared very soon after the first, showed that the author had already grasped the importance of his discovery.

The combining power of carbon has shown itself to be remarkable in every way. Standing as it does in the middle of the first short series of the Periodic Classification, it was to be expected that carbon would exhibit a disposition to unite with almost any element, irrespective of its electrochemical character. This expectation has been realized to a remarkable degree.

No less astonishing is the power of the carbon atoms to unite among themselves. This is well illustrated by the hydrocarbons known as paraffins. Dimyricyl is a solid, melting at 102°, and contains no fewer than sixty atoms of carbon united in one long continuous chain. The formula is therefore

$$CH_3(CH_2)_{58}CH_3$$

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[1] Kekulé, *Annalen*, 1857, **104**, 129.

[2] Kolbe, *J. pr. Chem.*, 1881, (11) **23**, 366.

[3] Frankland, *Proc. Roy. Soc.*, 1865, **14**, 198.

[4] Kolbe, *Annalen*, 1857, **101**, 262. This paper bears the name of Kolbe only, but purports to be a joint production. The name of Frankland appears to have been omitted by mistake.

A very interesting series of dibasic acetylenic acids was investigated by Baeyer[1] which illustrates still more forcibly the power of the carbon atoms to unite amongst themselves. The potassium salt of diacetylenedicarboxylic acid is obtained, together with copper oxide, by the oxidizing action of potassium ferricyanide upon the copper derivative of potassium propiolate. Thus:

$$(\mathrm{COOK}\,.\,\mathrm{C}\vdots\mathrm{C})_2\,.\,\mathrm{Cu} \rightarrow \mathrm{COOK}\,.\,\mathrm{C}\vdots\mathrm{C}\,.\,\mathrm{C}\vdots\mathrm{C}\,.\,\mathrm{COOK}$$

The potassium hydrogen salt of this acid on digestion with water loses carbon dioxide, whereby the potassium salt of diacetylene monocarboxylic acid results, namely—

$$\mathrm{COOK}\,.\,\mathrm{C}\vdots\mathrm{C}\,.\,\mathrm{C}\vdots\mathrm{C}\,.\,\mathrm{K}$$

This yields a copper compound, which, when oxidized by potassium ferricyanide, gives rise to the potassium salt of the highly explosive tetra-acetylenedicarboxylic acid,

$$\mathrm{COOK}\,.\,\mathrm{C}\vdots\mathrm{C}\,.\,\mathrm{C}\vdots\mathrm{C}\,.\,\mathrm{C}\vdots\mathrm{C}\,.\,\mathrm{C}\vdots\mathrm{C}\,.\,\mathrm{COOK}$$

No other element is known to form such peculiar compounds.

Very remarkable is the constancy of the valency exhibited by carbon. It is largely due to this property that the application of the theory of valency to the study of organic chemistry has met with such unparalleled success. In marsh gas, CH_4, carbon tetrafluoride, CF_4,[2] as well as in a host of complex derivatives whose constitutions have been determined within the last few years, carbon seems to function uniformly as a tetravalent element.

For many years carbon monoxide, $C = O$, was believed to contain divalent carbon, for the valency of oxygen was regarded as invariably two. Both Kekulé and Kolbe agreed on this point.[3] It was believed, however, that the two other valencies saturated themselves. The discovery of Collie and Tickle,[4] however, that oxygen can function as a tetravalent atom, renders the above assumption doubtful.[1] Nevertheless, many chemists are prepared to agree with Nef,[2] Gattermann,[3] Scholl,[4] and others, in regarding carbon as truly divalent in hydrocyanic acid, $\mathrm{C = N{-}H}$, isonitriles, $\mathrm{C = N{-}R}$, and fulminic acid $\mathrm{C = N{-}O{-}H}$.

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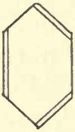
[1] Baeyer, *Ber.*, 1885, **18**, pp. 678 and 2269.

[2] Moissan, *Compt. rend.*, 1890, **110**, 276 and 951.

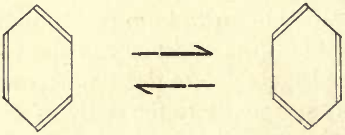
[3] Kolbe, *J. pr. Chem.*, **17**, 146.

[4] Collie and Tickle, *Trans. Chem. Soc.*, 1899, **75**, 710.

As is well known, the great difficulty of accepting Kekulé's formula for benzene, in which the carbon is represented as tetravalent, is the fact that it is not symmetrical. Thus:



We may, of course, overcome this objection by assuming with its author that the double bonds are continually changing their positions, so that a symmetrical figure is virtually obtained, as we have equilibrium between the two schemes:



In triphenylmethyl, $\mathrm{C(C_6\,H_5)_3}$, discovered by Gomberg[5] in 1900, carbon appears at the first blush to function as a trivalent element. This remarkable compound is prepared by the action of zinc on a benzene solution of triphenylchloromethane:

$$\mathrm{Zn + 2Cl \cdot C\,(C_6H_5)_3 = ZnCl_2 + 2C\,(C_6H_5)_3}$$

The triphenyl methyl is precipitated by acetone. It combines rapidly with iodine, giving triphenyliodomethane, $C(C_6H_5)_3I$. With oxygen a peroxide is formed, to which the formula

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[1] Compare Friend, *Trans. Chem. Soc.*, 1908, **93**, 269.

[2] Nef, *Annalen*, **270**, 286.

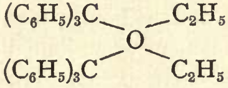
[3] Gattermann, *Ber.*, 1898, **31**, 1149.

[4] Scholl, *Ber.*, 1890, **23**, 3506; 1899, **32**, 3492.

[5] Gomberg, *Ber.*, 1900, **33**, 3150; 1901, **34**, 2726; 1902, **35**, 2397; 1903, **36**, 376 and 3928; 1904, **37**, 1626. *Amer. Chem. Journ.*, 1901, **25**, 317.

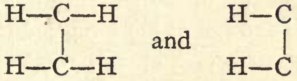
$$C(C_6H_5)_3—O—O—C(C_6H_5)_3$$

is given. With ether a compound of tetravalent oxygen is produced, thus:



In all these reactions the carbon functions as an unsaturated atom. That it is truly trivalent is open to doubt. There is reason to believe that the formula for triphenylmethyl is $[C(C_6H_5)_3]_2$, but we do not at present know how the atoms are arranged. Several constitutional formulæ have been proposed, but the question is by no means settled.[1]

In ethylene, C_2H_4, and acetylene, C_2H_2, carbon may be considered as trivalent and divalent respectively. Thus:



$$\begin{array}{ccc} H— & C & —H \\ & | & \\ H— & C & —H \end{array} \quad \text{and} \quad \begin{array}{cc} H— & C \\ & | \\ H— & C \end{array}$$

This difficulty is usually overcome by putting a double bond between the two carbon atoms in the case of ethylene, and a triple bond in the case of acetylene. Hinrichsen[2] takes exception to the assumption of double and triple bonds, and prefers to write ethylene and acetylene as above, regarding the valency of carbon as truly variable. His reasons may be stated as follows:—

1. According to Baeyer's theory of strain, one is led to expect in acetylene a very unstable gas. Yet at the high temperature of the electric arc this gas is apparently very stable. This is also true of the carbides of the metals

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[1] See Heintschel, *Ber.*, 1903, **36**, 320 and 579; Tschitschibabin, *Ber.*, 1904, **37**, 4709; 1907, **40**, 367; 1908, **41**, 2421; *J. pr. Chem.*, 1906, (2) **74**, 340; K. Auwers, *Ber.*, 1907, **40**, 2159; Gomberg, *Ber.*, 1907, **40**, 1847; 1906, **89**, 1318; 1905, **38**, 1333; Schmidlin, *Ber.*, 1907, **40**, 2316; 1908, **41**, 426 and 2471; Jacobson, *Ber.*, 1905, **38**, 196.

[2] Hinrichsen, *Zeit. phys. Chem.*, 1902, **39**, 305; *Annalen*, 1904, **336**, 175.

generally, which, as is well known, require a high temperature for their formation.

2. Certain physical constants, such as, for example, the molecular volume, are greater in bodies possessing a double bond, than in those which possess only single linkings. This is directly opposite to what we should expect, for when two atoms are joined by double bonds, we naturally assume that they lie nearer together than when joined by single linkings.

As Hinrichsen himself points out, his position is not unassailable. If carbon can function as a di- and tri-valent atom, we are led to ask why it is that such molecules as CH_2 and CH_3 are apparently unable to exist. But although no answer is forthcoming, it may be argued with justness, that this objection is equally applicable to the generally accepted theory of valency as applied to the other elements. Thus, for example, in nitric oxide, NO, the nitrogen may be regarded either as divalent or tetravalent, according as we attribute to oxygen a valency of two or four. Nevertheless, such hydrides as NH_2 and NH_4 have not as yet admitted of isolation.

It is not easy to see, however, what is gained by thus attributing to carbon a variable valency. By assuming its constancy, the study of organic chemistry has made unprecedented strides during the last quarter of a century. A theory of variable valency would, on the other hand, have caused no little confusion by greatly increasing the number of possible schemes which might be drawn up to represent complex organic bodies. Until some decided advantage is to be reaped by adopting the views which Hinrichsen so warmly supports, it would seem more advisable to adhere to the older theory.

We have no evidence that carbon ever functions as an element with a greater valency than four. Landolph[1] prepared $C_3H_6O . HF$, and $C_3H_6O . 2HF$, by the action of water on fluorboracetone, and suggests that we have here a hexavalent carbon atom. Hinrichsen[2] takes exception to this view and suggests that the former compound is represented by the formula

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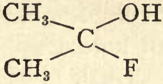
[1] Landolph, *Compt. rend.*, 1878, **86**, 1463; 1883, **96**, 580; *Jahresber.*, 1878, 320; 1883, 1298.

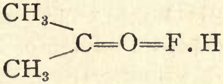
[2] Hinrichsen, *Ueber den gegenwärtigen Stand der Valenzlehre*, Stuttgart, 1902, p. 61.



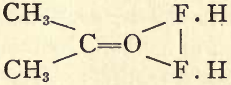
But why not assume that the fluorine is trivalent?—as is almost certainly the case in hydrofluoric acid, which consists of the double molecules [1]

$$H—F=F—H$$

The formulæ for the above compounds then become



and



In triphenylbromomethane tetra-iodide,[2] $(C_6H_5)_3CBrI_4$, carbon might appear to be functioning as an octavalent atom. By assuming, however, that bromine and iodine are trivalent, this difficulty is easily surmounted. A similar explanation applies to methyl iododichloride,[3] CH_3ICl_2, and to all other bodies of like composition.

Having now definitely determined the numerical value of the valency of the carbon atom, it was important to discover if the valencies were all of equal value. Popoff[4] proved the equality of the two unsaturated valencies in carbon monoxide. He allowed zinc methyl to act on caproyl chloride, whereby methyl amyl ketone was produced. Thus:

$$2C_5H_{11}COCl + Zn(CH_3)_2 = 2C_5H_{11}COCH_3 + ZnCl_2$$

This body was found to be identical with that produced by the action of zinc amyl on acetyl chloride. Thus:

$$2CH_3COCl + Zn(C_5H_{11})_2 = 2CH_3COC_5H_{11} + ZnCl_2$$

Geuther[5] and his pupils have made an extensive study of the formic esters, and have demonstrated the equality of the four carbon valencies.

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[1] See Chapter XV.

[2] Gomberg, *J. Amer. Chem. Soc.*, 1898, **20**, 790.

[3] Thiele and Peter, *Ber.*, 1905, **38**, 2842.

[4] Popoff, *Annalen*, 1868, **145**, 283.

[5] Geuther, *Annalen*, 1880, **205**, 223 and 227; 1883, **218**, 12; 1887, **240**, 192 and 225.

Henry[1] attacked the problem from an entirely different standpoint. He prepared nitromethane in four different ways, so that the nitro-group should, in each case, replace a fresh hydrogen atom. In order to explain the principle on which he worked, we will represent methane as

$$C\,H_a\,H_b\,H_c\,H_d$$

Beginning with methyl iodide,

$$C\,I\;\;H_b\,H_c\,H_d$$

which results by replacing one of the hydrogen atoms, say the *a*-atom, in methane by iodine, he converted a portion of it into nitromethane direct. This was therefore *a*-nitromethane,

$$C\,(NO_2)_a\,H_b\,H\;\;H_d$$

The remaining portion of methyl iodide was converted into the cyanide, saponified and chlorinated, whereby

$$C\,(COOH)_a\,Cl_b\,H_c\,H_d$$

resulted. The chlorine in a part of this was now replaced by a nitro-group, and the carboxyl group split off, whereby *b*-nitromethane resulted,

$$C\,H_a\,(NO_2)_b\,H_c\,H_d$$

In a similar manner the *c*- and *d*-nitromethanes were prepared. Since all these four nitromethanes were found to be identical in every respect, it is natural to argue that the same is true of the four carbon valencies.

It now behoves us to discover in which direction these valencies act.

The simplest arrangement would obviously be that of a square, containing a carbon atom at its centre, whilst towards its four corners the valencies of the carbon might be supposed to act. But this at once leads us into difficulties. According to this scheme we ought to be able to prepare two isomeric bodies, each having the formula CH_2Cl_2. Thus :

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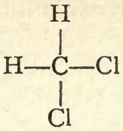
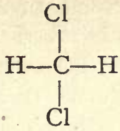
[1] L. Henry, *Compt. rend.*, 1887, **104**, 1106; *Zeit. phys. Chem.*, 1888, **2**, 553; *Jahresber*, 1886, 34; see *Bull. Acad. roy. Belg.*, 1906, 722.



$$\begin{array}{c} H \\ | \\ H—C—Cl \\ | \\ Cl \end{array}$$

and

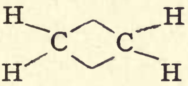


$$\begin{array}{c} Cl \\ | \\ H—C—H \\ | \\ Cl \end{array}$$

But this is contrary to experience. We are therefore forced to the conclusion that the directions in which the valencies act do not lie in one plane.

As early as 1869 Paternó[1] pointed out that if *three* isomeric forms of the compound $C_2H_4Br_2$ actually existed, an explanation could be found in the assumption that the four valencies of the carbon atom are directed towards the corners of a tetrahedron. Five years later, namely in 1874, Le Bel and van't Hoff advanced the same idea simultaneously, although each investigator had evidently arrived at it quite independently. The views were put forward in order to explain the optical isomerism of the lactic and tartaric acids.

Van't Hoff[2] evidently regards the carbon atom as a material point, at the centre of a tetrahedron, towards the corners of which its valencies are supposed to act. As Auwers[3] has pointed out, however, such a conception is beset with difficulties. In ethylene, for example, the double bond between the two carbon atoms is represented by the following scheme:—



We have here two sets of two forces, each set acting from two points, in such a way that all the forces are inclined to one another, no two acting in the same straight line. This implies that the valencies possess a definite direction and position in space, an assumption which attributes to mere forces properties which they cannot possess.[1]

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[1] Paternó was not the first to suggest a tetrahedral arrangement for the carbon atom. This honour belongs to Kekulé (see p. 49). Paternó's merit lay in first making the assumption that the four valencies are *directed towards the corners* of a tetrahedron.

[2] Van't Hoff, *La Chimie dans l'Espace*, 1874.

[3] Auwers, *Die Entwickelung der Stereochemie*, 1890.

Le Bel, on the other hand, has adopted a very different view. He[2] assumes that each atom possesses a definite sphere of attraction. If two such spheres intersect, their atoms are drawn together. A new repulsive force now comes into play, and when these two opposing forces exactly counteract one another, the atoms remain relatively at rest. Any three such atoms would clearly arrange themselves at the angles of an equilateral triangle.

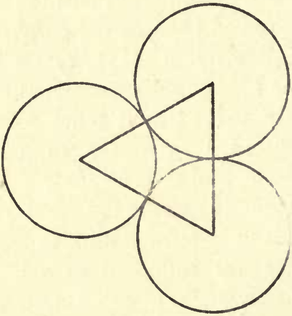

FIG. 1.

A fourth atom would complete the tetrahedral figure. The carbon atom is supposed to be inside the tetrahedron, and its sphere of repulsion to be bounded by the sides of the same. Knoevenagel[3] is inclined to assume that whilst the carbon atom has a tetrahedral form, its valencies are directed to the middle of the sides of the tetrahedron, and not to the corners. Hinrichsen[4] adopts this view, and uses it in support of his contentions against the theory of double bonds in unsaturated carbon compounds. The so-called double bonds are regarded as simply expressing the union of two carbon atoms along a common edge.

[1] Compare Lossen, *Annalen*, 1880, **204**, 336; *Ber.*, 1887, **20**, 3306.

[2] Le Bel, *Bull. Soc. chim.*, 1890, (3) **3**, 788.

[3] Knoevenagel, *Annalen*, 1900, **311**, 194.

[4] Hinrichsen, *Annalen*, 1904, **336**, 175.

It is interesting in this connection to call to mind the model of the carbon atom invented by Kekulé in 1867, two years before Paternó first published his suggestion to which reference has already been made.[1] The atom itself is regarded as a sphere, and from it project the four units of affinity "in the direction of hexahedral axes, so that they end in the faces of a tetrahedron."

According to Meyer,[2] "the carbon atom is surrounded by an ethereal shell, which, in the case of an isolated atom has a spherical form; the atom itself is the carrier of the specific affinities, the surface of the shell is the seat of the valencies; each affinity is determined by the existence of two opposite electrical poles which are situated at the end-points of a straight line small in comparison with the diameter of the ethereal shell. Such a system of two electric poles is called a double- or di-pole. The four valencies of a carbon atom would be represented by four such di-poles, the middle points of which are situated on the surface of the ethereal shell, but freely movable within it. The di-poles themselves can rotate freely round their middle point. The carbon atom has a greater attraction for positive than for negative electricity, and the positive pole of a valency is slightly stronger than the negative pole. This hypothesis explains why the four valencies take up the position of a regular tetrahedron; why they can be diverted from this position; why the valencies of one and the same carbon atom cannot combine together, whilst the valencies of different carbon atoms can do so; why there are two kinds of single binding, one stable, and the other allowing free rotation; and lastly, why free rotation ceases in cases of double- or treble-binding." [3]

Werner's[4] assumption is exceedingly simple. He fixes the valency of carbon as four, simply because no compound is known in which one carbon atom is united directly to more

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[1] Kekulé, *Zeit. Chem.*, 1867, N. F. **3**, 217; see *Kekulé Mem. Lect.*, Japp, 1897, p. 132.

[2] V. Meyer and Riecke, *Ber.*, 1888, **21**, 946.

[3] *Victor Meyer Mem. Lect.*, Thorpe, 1900, p. 193.

[4] Werner, *Beiträge zur Theorie der Affinität und Valenz*, 1891.

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than four other atoms. He does not regard valency, however, as dependent upon any one atom alone, but rather upon all the atoms in the molècule as a whole. Chemical affinity is assumed to be a force acting from the centre of an atom towards any and every point on the surface of a sphere at whose centre the atom lies. If all the atoms are spherical, any four attaching themselves to an atom of carbon will take up positions in the corners of a tetrahedron, at whose centre the carbon lies, for this is the only symmetrical grouping possible.

Many other suggestions[1] have been put forward from time to time by different investigators, but a full treatment of these is beyond the scope of this work. The reader desirous of pursuing the subject further is referred to Dr. Stewart's text-book on *Stereochemistry* (this series).

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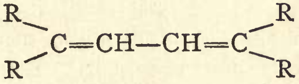
[1] Wunderlich, *Konfiguration organischer Moleküle*, 1886. Wislicenus, *Ber.*, 1888, **21**, 581. Sachse, *Ber.*, 1888, **21**, 2530; *Zeit. phys. Chem.*, 1893, **11**, 185. Naumann, *Ber.*, 1890, **23**, 477. Auwers, *Die Entwickelung der Stereochemie*, 1890, p. 31. Knorr, *Annalen*, 1894, **279**, 202. Vaubel, *Chem. Zeit.*, 1897, **21**, 96. Erlenmeyer, junior, *Annalen*, 1901, **316**, 71. Vorländer, *Annalen*, 1902, **320**, 99. Vorländer and Mumme, *Ber.*, 1903, **36**, 1470. E. Bloch, *Theorie des Kohlenstoffatoms*, Wien and Leipzig, 1903. de Heen, *Bull. Acad. roy. Belg.*, 1904, p. 285.

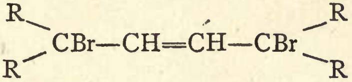
VII

THIELE'S THEORY

J. Thiele[1] has studied compounds of the type



and concludes that the double bonds do not represent complete saturation of the valencies of the atoms, but that each atom possesses a partial valency in addition. In this way he finds an explanation for the fact that bromination of the above group gives a double bond *in the middle*. Thus:



An exactly similar alteration in the position of the double bond takes place when such a system is reduced. For example, muconic acid,

$$COOH-CH{=}CH-CH{=}CH-COOH$$

when treated with sodium amalgam does not yield $\alpha\beta$ hydromuconic acid,

$$COOH-CH{=}CH-CH_2-CH_2-COOH$$

as we might expect, but the $\alpha\delta$ acid,

$$COOH-CH_2-CH{=}CH-CH_2-COOH$$

Baeyer[2] has observed similar behaviour amongst the aromatic acids.

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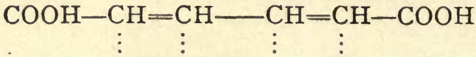
[1] Thiele, *Annalen*, 1899, **306**, 87; **308**, 213.

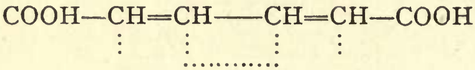
[2] Baeyer, *Annalen*, 1889, **251**, 271.

In order to represent this partial valency, Thiele proposes the use of dotted lines. Thus muconic acid is written



$$\mathrm{COOH}{-}\underset{\vdots}{\mathrm{CH}}{=}\underset{\vdots}{\mathrm{CH}}{-\!\!-}\underset{\vdots}{\mathrm{CH}}{=}\underset{\vdots}{\mathrm{CH}}{-}\mathrm{COOH}$$

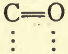
A group containing two adjoining pairs of double bonds, is known as a conjugated system, and it is regarded as probable that the two middle partial valencies saturate each other. Thus—



$$\mathrm{COOH}{-}\underset{\vdots}{\mathrm{CH}}{=}\underset{\vdots}{\mathrm{CH}}{-\!\!-}\underset{\vdots}{\mathrm{CH}}{=}\underset{\vdots}{\mathrm{CH}}{-}\mathrm{COOH}$$

This leaves the α and δ carbon atoms unsaturated, and on reduction or bromination, the hydrogen or bromine atoms combine with these, rather than with the $\beta\gamma$ atoms. The partial valencies of the latter now become ordinary, thus giving rise to a double bond in the middle, and the double bonds disappear from the two sides.

According to this notation, the formula for carbon monoxide becomes



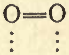
$$\underset{\vdots}{\mathrm{C}}{=}\underset{\vdots}{\mathrm{O}}$$

which represents the ease with which it undergoes oxidation.

It is now well known that, in many cases of oxidation, the oxygen molecule as a whole combines with the oxidizable substance. For example, Engler and Wild[1] show that such is the case when the alkali metals are oxidized in the air, for a peroxide is invariably first formed. Thus:

$$2\mathrm{Na} + \mathrm{O}_2 = \mathrm{Na}_2\mathrm{O}_2$$

Adopting Thiele's notation for the oxygen molecule,



$$\underset{\vdots}{\mathrm{O}}{=}\underset{\vdots}{\mathrm{O}}$$

it is easy to see why this should be the case.

It is, however, when applied to the study of aromatic compounds that Thiele's theory becomes most interesting. There is the perennial problem as to the graphical formula of benzene.

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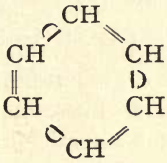
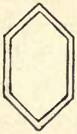
[1] Engler and Wild, *Ber.*, 1897, **30**, 1669; but see p. 100.

Whilst that suggested by Kekulé (p. 42) is very satisfactory for all ordinary purposes, we are bound to assume with its inventor that the positions of the double bonds continually alternate, otherwise we are faced with the difficulty that the molecule is not symmetrical, and two isomeric ortho disubstitution products are to be expected.

According to Thiele's theory the formula is



where the curved lines indicate the partial valencies. If all the bonds are regarded as equivalent, the formula becomes



and this is symmetrical. Since the partial valencies have here neutralized one another, the molecule is not to be regarded as unsaturated. This is in harmony with the character of the benzene molecule.

Whilst Thiele's theory explains many reactions upon which the generally accepted views on valency can throw no light, a large number of facts has been accumulated, which cannot be reconciled with it.

Harries,[1] for example, finds that unsaturated ketoximes and aldoximes can be reduced to unsaturated amines, and that acrolein derivatives can also be converted by the aluminium-mercury couple into monohydric alcohols. Erlenmeyer junior[2] has drawn attention to the fact that when cinnamylformic acid

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[1] Harries, *Annalen*, 1904, **330**, 185.

[2] Erlenmeyer, junior, *Ber.*, 1903, **36**, 2527 ; 1904, **37**, 1318.

$$C_6H_5—CH{=}CH—CO—COOH$$

is reduced, it is the ketone group which is attacked, and the $\beta\gamma$ unsaturated hydroxy acid results—

$$C_6H_5—CH{=}CH—CHOH—COOH$$

Hinrichsen points out that all the advantages of Thiele's theory are reaped if we assume that no double bonds can exist, but that the valencies of the carbon atom lie unsaturated. For muconic acid he would therefore write

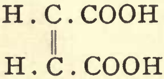
$$COOH—CH—CH—CH—CH—COOH$$

in which the four middle carbon atoms are trivalent. If now two similar atoms, for example bromine or hydrogen, are added to this system, we might naturally expect them to take up positions as far from one another as possible. Thus:

$$COOH—CH_2—CH—CH—CH_2—COOH.$$

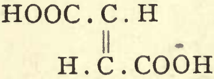
If, on the other hand, dissimilar atoms are added, or, as in the cases quoted by Harries and Erlenmeyer, the molecules are not symmetrical, we must look for a different arrangement.

But Hinrichsen's position is open to criticism. If we do not recognize the existence of double bonds, how are we to account for the isomerism exhibited by maleic and fumaric acids, to which the formulæ



$$\begin{array}{l} \mathrm{H\,.\,C\,.\,COOH} \\ \quad \| \\ \mathrm{H\,.\,C\,.\,COOH} \end{array}$$

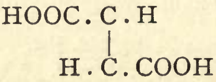
and



$$\begin{array}{l} \mathrm{HOOC\,.\,C\,.\,H} \\ \qquad\quad \| \\ \qquad \mathrm{H\,.\,C\,.\,COOH} \end{array}$$

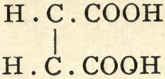
have been ascribed respectively?

If we adhere to van't Hoff's conception that the valencies of the carbon atom are directed towards the corners of a tetrahedron, we shall have to seek an explanation for the above, entirely different from that usually accepted. If the carbon is merely trivalent there is no reason why



$$\begin{array}{l} \mathrm{HOOC\,.\,C\,.\,H} \\ \qquad\quad | \\ \qquad \mathrm{H\,.\,C\,.\,COOH} \end{array}$$

should not be perpetually swinging round to



$$\begin{array}{c}\mathrm{H\,.\,C\,.\,COOH}\\ |\\ \mathrm{H\,.\,C\,.\,COOH}\end{array}$$

and *vice versâ*, or be taking up a score of intermediate positions.

Hinrichsen points out that this difficulty is removed if we assume with Knoevenagel[1] that the carbon valencies are directed towards the *centre* of the faces of the tetrahedron representing the atom. The so-called double bond is thus the union of two atoms along a common edge.

A full account of Werner's theory of double bonds may be found in Stewart's *Stereochemistry* (this series).

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[1] Knoevenagel, *Annalen*, 1900, **311**, 194.

VIII

THE VALENCY OF THE ELEMENTS OF GROUP O

The elements of this group, the so-called inert or noble gases, seem to be entirely devoid of chemical affinity or valency, for not only do they seem incapable of combining with themselves to form polyatomic molecules, but they are remarkably inactive towards all the other known elements. The name "argon" or "idle" is well adapted to the behaviour of the gas so christened, and would apparently apply with equal aptness to the other inert gases, namely helium, neon, krypton, and xenon.

The fact that argon can be separated from oxygen and nitrogen by exposing the mixed gases to a rain of electric sparks, shows that it cannot be made to combine with one of the most electronegative of elements, namely oxygen. Red-hot magnesium, as strongly positive as oxygen is negative, has likewise no action on the gas. Sparking with hydrogen or chlorine yields no result, and the vapours of sulphur, phosphorus, sodium, and tellurium in red-hot tubes are also without effect. Combination could not be observed even when argon was subjected to the several action of red-hot sodium hydroxide, sodium and potassium persulphides, nascent chorine, and even of fluorine[1] itself.

It is true that when an electric arc was formed between carbon electrodes in an atmosphere of argon, a slight expansion was observed, the final volume of gas being greater than the initial. Repetition of the experiment, however, showed that this was due to the formation of some oxide of carbon, owing to the presence of traces of oxygen adhering to the carbon rods. Treatment with ammoniacal cuprous chloride reduced it to its original value, and the argon was recovered unchanged.[1]

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[1] Moissan, *Compt. rend.*, 1895, **120**, 966.

On the other hand, Berthelot states, that, by exposing a mixture of benzene and argon to an electric discharge, a brown resinous mass is obtained, covering the walls of the tube.[2] A similar reaction takes place if carbon bisulphide is used instead of benzene. Whether or no this may be regarded as a case of true chemical combination is doubtful.[3] Berthelot obtained similar results with helium.

Ternent Cooke[4] has recently determined the vapour density of zinc in an atmosphere of argon, and finds it to be 12% higher than in nitrogen. He concludes, therefore, that zinc and argon exhibit a distinct tendency to form a compound. The same tendency is also manifested by cadmium and helium, mercury and argon, mercury and helium, and to a less extent by selenium and argon, and by selenium and helium. For the present, however, the inert gases must be regarded as devoid of chemical affinity in the ordinary acceptation of the term.

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[1] Ramsay and Collie, *Chem. News*, 1896, **73**, 259; *Proc. Roy. Soc.*, 1896, **60**, 53.

[2] Berthelot, *Compt. rend.*, 1895, **120**, 581, 660 and 1316.

[3] Berthelot, *Compt. rend.*, 1897, **124**, 113.

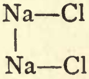
[4] T. Cooke, *Zeit. phys. Chem.*, 1906, **55**, 537.

IX

THE VALENCY OF THE ELEMENTS OF GROUP I

As a rule the alkali metals are regarded as monovalent. This view was apparently justified when their hydrides were prepared, namely lithium hydride, LiH, by Guntz in 1893, and the following by Moissan—sodium hydride, NaH (1901); potassium hydride, KH (1902); rubidium and cæsium hydrides, RbH and CsH (1903).

J. Traube[1] concludes that the molecule of sodium chloride in solution is double. If we accept this view and postulate the strict monovalency of chlorine, we are bound to assume that sodium is at least divalent. The graphical formula for sodium chloride thus becomes



$$\begin{array}{l}\mathrm{Na{-}Cl}\\ \;\,|\\ \mathrm{Na{-}Cl}\end{array}$$

As we shall see later, however, it is more reasonable to assume that the chlorine is trivalent, thus:

$$\mathrm{Na{-}Cl{=}Cl{-}Na}$$

Geuther,[2] after studying the polysulphides of the alkali metals, came to the conclusion that the latter could function as tri- and penta-valent atoms.

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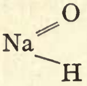
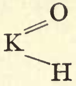
[1] See Hinrichsen, *Ueber den gegenwärtigen Stand der Valenzlehre*, Stuttgart, 1902, p. 54.

[2] Geuther, *Jenaische Zeitsch*, (2) **6**, 1 Suppl., p. 119.

Wanklyn[1] believes that the graphical formulæ for sodium and potassium hydroxides are



and



in which both metals are trivalent. Köhler[2] takes exception to this view, however. In the potassium hydrogen fluorides, KHF_2, KH_2F_3, and KH_3F_4, potassium is not to be regarded as tri-, penta-, and hepta-valent respectively. The halogen is here trivalent, the formula for the first complex being

$$K—F=F—H$$

The correctness of this view is shown by the fact that hydrofluoric acid is largely associated to double molecules,[3] H_2F_2, for which the formula

$$H—F=F—H$$

seems most probable, since hydrogen is never known to function as a divalent atom.

The condition of iodine and bromine dissolved in solutions of potassium iodide and bromide has been the subject of many researches.[4] Sufficient evidence has been forthcoming to justify us in the belief that the complexes KI_3 and KBr_3 are capable of formation. To assume, however, that the metals are trivalent in these compounds would be incorrect. Wells and Wheeler[5] have prepared and studied the mixed halogen compounds of rubidium and cæsium, as for example rubidium chlorobromide, $RbClBr_2$. The existence of such complexes would seem to indicate that we are here dealing with so-called molecular compounds, and that the bromine is not attached directly to the metal, but to the chlorine. Thus:

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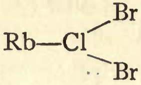
[1] Wanklyn, *Ber.*, 1869, **2**, 64; *Trans. Chem. Soc.*, 1869, **7**, 199.

[2] Köhler, *Ber.*, 1870, **3**, 235; see Gerstl, *Ber.*, 1870, **3**, 102.

[3] See Mallet, *Chem. News*, 1881, **44**, 164; compare Vernon, *Chem. News*, 1891, **64**, 54; Thorpe and Hambly, *Trans. Chem. Soc.*, 1889, **55**, 163; see also Chapter XVI., where full references are given.

[4] See Johnson, *Trans. Chem. Soc.*, 1877, **31**, 249; Jakowkin, *Zeit. phys. Chem.*, 1894, **13**, 529; 1896, **20**, 14. Dawson and his co-workers, *Trans. Chem. Soc.*, 1901, **79**, 238; 1902, **81**, 524; 1904, **85**, 796; 1908, **93**, 1308; Lachmann, *J. Amer. Chem. Soc.*, 1903, **25**, 50; Worley, *Trans. Chem. Soc.*, 1905, **87**, 1107.

[5] Wells and Wheeler, *Zeit. anorg. Chem.*, 1892, **1**, 85 and 442; 1892, **2**, 255.

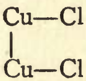


The formulæ for potassium tribromide and tri-iodide are probably similar to this.

Abegg and Hamburger[1] have recently studied the polyiodides of the alkali metals, and have demonstrated the existence of the following complexes: CsI, CsI_3, CsI_5 or CsI_7, CsI_9, RbI, RbI_3, RbI_7, and RI_9. It is unnecessary to assume, however, that the metals are other than monovalent.

Many metals are capable of forming two entirely different classes of salts. Copper is a case in point. It unites, for example, with chlorine in two proportions, forming cupric chloride, $CuCl_2$, and cuprous chloride, which latter contains one atom of chlorine to every atom of copper.

According to the doctrine of constant valency, cuprous chloride should have the formula



$$\begin{array}{l}\mathrm{Cu—Cl}\\ \,|\\ \mathrm{Cu—Cl}\end{array}$$

whereby copper still retains its divalent character. This was believed to be supported by the results of vapour density determinations effected by Biltz and V. Meyer,[2] and by V. Meyer and C. Meyer.[3] These investigators found that the vapour density of cuprous chloride at 1600–1700° C. was approximately 6·5 (air = 1). That calculated for the formula Cu_2Cl_2 is 6·83. This remarkable agreement leaves no room for doubt that in the gaseous condition the salt is correctly represented by the double formula.

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[1] Abegg and Hamburger, *Zeit. anorg. Chem.*, 1906, **50**, 403. See also Foote and Chalker, *Amer. Chem. J.*, 1908, **39**, 561.

[2] Biltz and V. Meyer, *Ber.*, 1889, **22**, 725.

[3] V. Meyer and C. Meyer, *Ber.*, 1879, **12**, 609, 1112, 1185 and 1292.

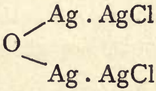
In 1897, however, Werner[1] determined the molecular weights of a number of salts dissolved in various organic solvents, as, for example, pyridine and piperidine. The results showed that in such circumstances the molecule of cuprous chloride is single, and is hence correctly represented by the formula CuCl. Rügheimer and Rudolphi[2] have shown that the same is true for solutions in fused bismuth chloride (M.P. 225–230° C), and E. Beckmann and Gabel[3] have obtained similar results in a series of experiments carried out with quinoline as solvent, when the concentration of the copper salt was not too great. Copper must therefore be regarded as truly monovalent in cuprous salts, an assumption which justifies its inclusion in the first column of the Periodic Classification.

The fact that in the vaporous state the molecules of cuprous chloride are double is probably to be attributed to the trivalent nature of chlorine. Thus:

$$\mathrm{Cu{-}Cl{=}Cl{-}Cu}$$

Silver salts resemble those of monovalent copper in many of their chemical properties, and certain salts of the two elements are isomorphous.[4] Although two distinct classes of silver salts are not known, corresponding to those of copper, yet we have indications to prove that silver is not always monovalent.

It is well known that when silver chloride or bromide is exposed to the action of light and air, chemical change takes place, resulting in the formation of a dark substance. This of course lies at the very root of our photographical processes. The formula given by Hodgkinson to the dark body formed from silver chloride is Ag_4OCl_2, or



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[1] Werner, *Zeit. anorg. Chem.*, 1897, **15**, 565.

[2] Rügheimer and Rudolphi, *Annalen*, 1905, **339**, 311.

[3] Beckmann and Gabel, *Zeit. anorg. Chem.*, 1906, **51**, 236.

[4] Wislicenus, *Ber.*, 1871, **4**, 63; M. Traube, *Ber.*, 1886, **19**, 1117.

in which silver functions as a divalent atom.[1] Barbieri adduces further evidence in favour of divalent silver. In the suboxide, Ag_4O,[3] silver must be regarded as at least divalent, unless we assume that oxygen is tetravalent. Perhaps, however, this latter assumption is the more probable.

The last element of this group to be considered is gold. This metal resembles copper in its power of forming two distinct series of salts, namely aurous and auric. In the aurous salts, gold is monovalent; for example, aurous chloride, AuCl. In the auric salts, however, it is not divalent but trivalent, thereby differing from copper in the cupric salts. A further distinction lies in the tendency of gold to form complex salts, for example, potassium aurocyanide, $KAu(CN)_2$, and potassium aurichloride, $KAuCl_4$. In these bodies the gold appears to be tri- and penta-valent, respectively. If, however, we regard them as molecular compounds, and write their formulæ as

$$AuCN . KCN \quad \text{and} \quad AuCl_3 . KCl$$

it is clear that the gold may be merely functioning as a mono- and tri-valent atom, the (CN) in the former and the Cl in the latter having a greater valency than unity.

The recent discovery by Pope and Gibson[4] of di-ethyl auric bromide, $(C_2H_5)_2AuBr$, and mono-ethyl auric dibromide, $(C_2H_5)AuBr_2$, would appear to fix the trivalent nature of the auric atom.

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[1] See *The Chemistry of Photography*, Meldola, 1901, p. 57.

[2] Barbieri, *Atti R. Accad. Lincei*, 1907, (v.) **16**, ii. 72.

[3] Wöhler, *Annalen*, 1860, **114**, 119. But see Muthmann, *Ber.*, 1887, **20**, 983; Friedheim, *Ber.*, 1887, **20**, 2554; 1888, **21**, 307; Pillitz, *Zeit. anal. Chem.*, 1882, **21**, 27 and 496; Spencer Newbury, *Amer. Chem. J.*, 1886, **8**, 196; Pfordten, *Ber.*, 1887, **20**, 1458, and 3375; 1888, **21**, 2288; Bailey and Fowler, *Trans. Chem. Soc.*, 1887, **51**, 416.

[4] Pope and Gibson, *Trans. Chem. Soc.*, 1907, **91**, 2061.

X

THE VALENCY OF THE ELEMENTS OF GROUP II

THE valency of the first element of this group, namely glucinum, has already received full consideration in an earlier chapter.[1] Of the divalency of magnesium there can be no reasonable doubt. It is true that its salts show a great tendency to unite with water of crystallization. For example, from a solution of magnesium oxide or carbonate in hydrochloric acid, crystals of the composition $MgCl_2 . 6H_2O$ are deposited. In the presence of ammonium chloride the double salt $MgCl_2 . NH_4Cl . 6H_2O$ is formed, which may be dehydrated on heating without decomposition of the magnesium chloride. Further heating causes the volatilization of the ammonium chloride, leaving a mass of fused anhydrous magnesium chloride, $MgCl_2$, which congeals to a white crystalline solid. It is most probable that in all these compounds the magnesium is consistently divalent, but that the chlorine and oxygen are functioning as tri- and tetravalent atoms respectively.

Further evidence of the divalent nature of magnesium is afforded by its organic derivatives. Magnesium diphenyl,[2] $Mg(C_6H_5)_2$, is readily produced by heating mercury diphenyl with magnesium powder and some acetic ester to 180–185° C.

$$Mg + Hg(C_6H_5)_2 = Mg(C_6H_5)_2 + Hg$$

Magnesium phenyl bromide, $C_6H_5 . Mg . Br$, better known perhaps as Grigniard's reagent, is readily formed by the solution of magnesium ribbon in a mixture of bromobenzene and absolute ether.[1] A similar compound, namely, $C_2H_5 . Mg . Br$, is formed when magnesium is added to ethyl bromide in benzene solution. On warming magnesium filings with ethyl iodide in the absence of air, $C_2H_5 . Mg . I$ is formed, which, on being heated, decomposes into magnesium di-ethyl, $Mg(C_2H_5)_2$, and magnesium iodide, MgI_2.

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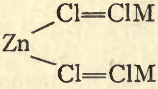
[1] See p. 25.

[2] Waga, *Annalen*, 1894, **282**, 329.

In all of these bodies magnesium is clearly divalent.

The divalency of zinc is confirmed by the existence of the well-known alkyl compounds, namely zinc dimethyl, $Zn(CH_3)_2$, etc., which have been used to such great advantage in synthetic organic chemistry. Should any other proof be necessary, it may perhaps be found in the isomorphism which exists to such a remarkable extent between the salts of zinc and magnesium.

Zinc chloride, $ZnCl_2$, unites with alkali chlorides to form a series of crystalline double salts, having the formula $ZnCl_2 . 2\,MCl$, where M stands for a monovalent metal. This is not to be attributed to the zinc functioning as a hexavalent atom. Rather is it to be ascribed to the trivalent nature of chlorine. Thus:



Kahan[2] has studied the action of zinc on ethyl iodide at temperatures of 100° and upwards. During the course of her experiments she observed that even when the zinc was in excess of that theoretically necessary for the complete decomposition of the iodide into butane according to the equation

$$Zn + 2IC_2H_5 = ZnI_2 + C_2H_5 . C_2H_5$$

still the greater the proportion of zinc employed, the greater was the amount of butane obtained. Kahan therefore suggests that part of the zinc, in addition to its two ordinary valencies, possesses an equal number of residual valencies. Thus :

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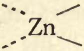
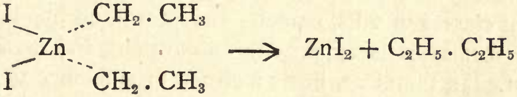
[1] Pfeiffer and Truskier, *Ber.*, 1904, **37**, 1125.

[2] Kahan, *Trans. Chem. Soc.*, 1908, **93**, 138.



where the dotted lines represent the residual valencies. On heating the zinc and ethyl iodide, therefore, di-ethyl di-iodide of zinc is formed as an unstable intermediate product, which spontaneously decomposes to zinc iodide and butane, according to the equation



As Kahan acknowledges, however, the assumption that zinc can behave as a tetravalent element is certainly unusual; but that in itself constitutes no argument against it. Until quite recently oxygen was regarded as invariably divalent, but we have now good reasons for assuming that it can also be tetravalent, as we shall see in a later chapter.

Cadmium so closely resembles zinc in its chemical behaviour that we should naturally expect it to behave as a divalent metal. This is, indeed, found to be the case. Nevertheless, evidence is forthcoming to show that it may also be monovalent. Although no subsalts are at present known, Tanatar and Levin[1] have obtained evidence in favour of the existence of a suboxide Cd_2O. They heated the basic oxalate and confirmed the constitution of the resulting suboxide by thermochemical measurements. Brislee[2] and Denham[3] have recently confirmed this result. The former studied the reduction of cadmium monoxide, CdO, by carbon monoxide. The time-reduction curve shows a distinct break at the point corresponding to the completion of reduction of the monoxide to the suboxide.

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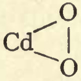
[1] Tanatar and Levin, *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 495.

[2] Brislee, *Trans. Chem Soc.*, 1908, **93**, 164.

[3] Denham, *Trans. Chem. Soc.*, 1908, **93**, 834.

Tanatar[1] has chronicled the preparation of Cd_4O, which he obtained by the cautious ignition of cadmium oxalate in a stream of carbon dioxide. This corresponds to silver suboxide Ag_4O,[2] and probably contains tetravalent oxygen. In cadmium peroxide, CdO_2,[3] we are probably dealing again with tetravalent oxygen. According to the generally accepted ideas, the formula might also be written



Mercury is characterized by its tendency to form two different classes of salts, namely, mercurous and mercuric salts. In the former it is apparently monovalent, and in the latter divalent. It, therefore, bears a strong resemblance to copper.

The study of the valency of mercury in calomel, in which one atom of the metal is attached to one of chlorine, has proved of no little interest. Mitscherlich[4] found that the vapour density of the salt corresponded to the formula HgCl, in which the molecules are single. The monovalency of mercury was, therefore, apparently established, especially as similar experiments by Deville and Troost,[5] and Rieth,[6] yielded almost identical results.

A new complexion was placed on the matter, however, when Odling[7] showed that on vaporization, calomel was dissociated into mercuric chloride, $HgCl_2$, and metallic mercury. This was demonstrated by the fact that, if a piece of gold leaf were suspended in the vapour, it amalgamated with the mercury and, on cooling, a residue of mercuric chloride was left. This result received confirmation at the hands of Erlenmeyer,[8] Debray,[9] and W. Harris and V. Meyer.[10] It

[1] Tanatar, *Zeit. anorg. Chem.*, 1901, **27**, 437.

[2] Wöhler, *Annalen*, 1860, **114**, 119 ; see p. 62.

[3] Manchot, *Ber.*, 1906, **39**, 170,

[4] Mitscherlich, *Pogg. Ann.*, **29**, 139.

[5] Deville and Troost, *Compt. rend.*, 1857, **45**, 821.

[6] Rieth, *Ber.*, 1870, **3**, 666.

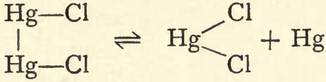
[7] Odling, *Quart. Journ. Chem. Soc.*, 1850, **3**, 211.

[8] Erlenmeyer, *Annalen*, 1864, **131**, 124.

[9] Debray, *Compt. rend.*, 1876, **83**, 330.

[10] W. Harris and V. Meyer, *Ber.*, 1894, **27**, 1482.

was clear, therefore, that this phenomenon could be better explained on the assumption that the salt really consists of double molecules, the change on vaporization being represented by the equation



Baker,[1] in a remarkable series of investigations, has shown that, if perfectly dry, calomel may be vaporized without decomposition, its density then corresponding to the double formula Hg_2Cl_2.

It is not improbable, however, that in the mercurous salts the metal is truly monovalent, just as copper appears to be in the cuprous salts. The association of mercurous chloride to double molecules in the vapour state, is to be attributed to the trivalent nature of chlorine, and the formula becomes

$$\mathrm{Hg{-}Cl{=}Cl{-}Hg}$$

In mercuric compounds, the metal is truly divalent. This is definitely proved by the organic derivatives. When sodium amalgam is allowed to act on bromobenzene, C_6H_5Br, in benzene solution, mercury diphenyl, $Hg(C_6H_5)_2$, is formed in colourless rhombic prisms, which turn yellow in sunlight.[2]

$$2C_6H_5Br + HgNa_2 = Hg(C_6H_5)_2 + 2NaBr$$

In this compound mercury is clearly divalent, as also in mercury di-ethyl, $Hg(C_2H_5)_2$, which admits of preparation in an analogous manner.[3]

With regard to calcium, strontium, and barium, there is little to be said, for each metal reacts uniformly as a divalent atom. Strontium ammonium decomposes slowly *in vacuo* at 20°, leaving a residue of strontium amide, $Sr(NH_2)_2$. By the action of carbon monoxide on strontium ammonium, a carbonyl derivative, $Sr(CO)_2$, is obtained.[4] In this latter compound strontium might be considered as tetravalent. It is more probable, however, that its molecule is represented by the scheme

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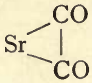
[1] Baker, *Trans. Chem. Soc.*, 1900, **77**, 646.

[2] See Otto and Dreher, *Annalen*, 1870, **154**, 93.

[3] Compare Buckton, *Proc. Roy. Soc.*, 1859, **9**, 309.

[4] Roederer, *Bull. Soc. chim.*, 1906, (iii.) **35**, 715.



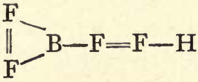
in which the metal appears as a divalent atom (compare nickel carbonyl).

XI

THE VALENCY OF THE ELEMENTS OF GROUP III

THE only non-metallic element of this group is boron, which is generally regarded as trivalent.

The fluoride[1] unites with a molecule of hydrofluoric acid to form hydrofluoboric acid, HBF_4, in which boron apparently functions as a pentavalent element. We have no proof, however, that such is the case, and, as we have already seen in an earlier chapter, fluorine is not always monovalent. It is not improbable, therefore, that hydrofluoboric acid is represented by the graphical formula



In boron trimethyl, $B(CH_3)_3$, and boron tri-ethyl, $B(C_2H_5)_3$,[2] the element is decidedly trivalent. But these bodies possess the power of combining with potassium hydroxide and with ammonia to form $B(CH_3)_3 : KOH$ and $B(CH_3)_3 : NH_3$, where boron is evidently pentavalent.

With regard to the valency of aluminium opinion seems to be divided. Buckton and Odling[3] showed that one atom of aluminium can combine with three methyl or three ethyl groups yielding alkyl derivatives, whose vapour consists of the simple molecules $Al(CH_3)_3$ and $Al(C_2H_5)_3$ respectively. In these compounds the valency of aluminium is obviously three.[1] Combes studied the aluminium derivatives of acetylacetone, and his results point to the same conclusion. Deville and Troost,[2] however, called attention to the fact that, in the vaporous condition, the halogen salts of aluminium consist of double molecules, thus: Al_2Cl_6, Al_2Br_6, and Al_2I_6. Friedel and Crafts[3] obtained similar results by employing Dumas' method at temperatures ranging from 218° to 432° C. Nilson and Pettersson,[4] however, pointed out that these results were only true at certain temperatures.

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[1] Gay Lussac and Thenard, *Ann. Chim. Phys.*, 1809, **69**, 204.

[2] Frankland, *Annalen*, 1862,**124**, 129 ; *Jahresber.*, 1876, p. 469 ; *Phil. Trans.*, 1862, **152**, 167.

[3] Buckton and Odling, *Annalen*, *Suppl.* (4), 112 ; *Proc. Roy. Soc.*, 1865, **14**, 19.

Whilst the density of aluminium chloride, as observed by Deville and Troost, is 9·20 between 350° and 440° C., exactly corresponding to that required for the double formula, at lower temperatures the density is greater, and less again at higher. It is clear, therefore, that the vapour of the salt at the lower temperatures consists of unstable associations of molecules, which gradually dissociate as the temperature rises, until at about 800° dissociation is complete. At this temperature the vapour density is 4·60, which is exactly the value calculated for the simple molecules $AlCl_3$. Above 800° the density remains constant as, indeed, we should expect. The equilibrium existing between the molecules below 800° may, therefore, be expressed by the equation

$$(AlCl_3)_n \rightleftharpoons n(AlCl_3)$$

Are we, however, to assume that in the double molecules, Al_2Cl_6, aluminium is functioning as an atom of higher valency than three?

Hinrichsen[5] answers this question in the affirmative, and suggests that the metal is either tetravalent or pentavalent. Thus:

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[1] At lower temperatures aluminium trimethyl exhibits a slight but decided tendency to associate to double molecules. See the criticism of Williamson, *Proc. Roy. Soc.*, **14**, 74.

[2] Deville and Troost, *Compt. rend.*, 1857, **45**, 821; *Ann. Chim. Phys.*, 1860 (3), **58**, 257.

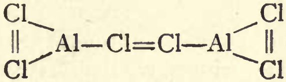
[3] Friedel and Crafts, *Compt. rend.*, 1888, **106**, 1764.

[4] Nilson and Pettersson, *Zeit. phys. Chem.*, 1887, **1**, 459; 1889, **4**, 206.

[5] Hinrichsen, *Ueber den gegenwärtigen Stand der Valenzlehre*, Stuttgart, 1902 p. 59.

$$\equiv\text{Al}-\text{Al}\equiv \quad \text{or} \quad \equiv\text{Al}=\text{Al}\equiv$$

It is more probable, however, that the halogens are the real cause of the association, just as was suggested in connection with cuprous and mercurous chlorides. The formula then becomes



and it is easy to see how association to still higher complexes can take place without attributing to aluminium a higher valency than three.

With regard to gallium chloride there was for several years a good deal of uncertainty.[1] Whilst some chemists regarded its molecule as double, namely Ga_2Cl_6, others maintained that it was more correctly represented by the single formula $GaCl_3$. This uncertainty arose from the fact that the vapour density determinations by Dumas' method always gave higher values than those obtained on Dulong's principle at the same temperatures.

An explanation for this apparent anomaly is to be found in the fact that dissociation depends not only upon temperature, but also upon pressure—as we should expect from the kinetic theory. Consequently dissociation is more advanced at a particular temperature when the salt is evaporated in an atmosphere of an indifferent gas, than is the case with the displacement method.

Nilson and Pettersson[2] showed that two chlorides of gallium exist in the vapour state, namely

$$GaCl_2 \quad \text{and} \quad GaCl_3.$$

This proves that gallium can act both as a divalent and as a trivalent atom.

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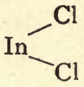
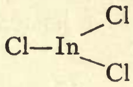
[1] See Lecoq de Boisbaudran, *Compt. rend.*, 1881, **93**, 329; Friedel and Crafts, *Compt. rend.*, 1888, **107**, 306.

[2] Nilson and Pettersson, *Zeit. phys. Chem.*, 1887, **1**, 459.

The case of indium is no less interesting. Victor Meyer[1] showed that when vaporized the molecules of its trichloride were single, namely $InCl_3$. Nilson and Pettersson extended these results[2] and made the discovery that no fewer than three chlorides of indium can exist in the gaseous state, namely

In—Cl,  and 

It is true that the mono- and di-chlorides are excessively unstable. In contact with water they form the trichloride, and indium is precipitated. Nevertheless they are true compounds and the metal is apparently functioning as a mono-, di-, and tri-valent atom respectively.

The last element of this group to be considered is thallium, discovered by Crookes in 1861. This metal resembles gold in that it is able to form two classes of salts, namely thallous and thallic, in which it functions as a monovalent and trivalent atom respectively. This is clear from a study of the chlorides. When hydrochloric acid is added to a solution of a thallous salt, a white, curdy precipitate of thallous chloride, TlCl, is obtained, reminding one very strongly of silver chloride. Here the atom is decidedly monovalent. Thallic chloride, $TlCl_3$, is formed by passing chlorine through water in which thallous chloride is suspended. On evaporation *in vacuo*, crystals of $TlCl_3 . 2H_2O$ are obtained. Here the thallium is clearly trivalent, unless indeed we assume that the water of crystallization is attached directly to the metal, when a still higher valency must be attributed to it. This is scarcely likely to be the case, however, for thallic nitrate can be deposited as colourless crystals containing no fewer than eight molecules of water. Thus:

$$Tl(NO_3)_3 . 8H_2O.$$

Maitland and Abegg[3] point out that the tri-iodide, TlI_3, may be regarded as a tautomeric substance since it reacts in solution either as a compound of monovalent thallium with the complex I_3 ion, or as an iodide of trivalent thallium, according to the nature of the substance with which it is brought into contact. From solubility considerations and the fact that a change in the composition of the solid substance in equilibrium with the solution produces only a comparatively small change in the thallous iodide concentration, it would appear that TlI_3 is essentially a thallous compound. This is in agreement with the observed isomorphism existing between thallium, rubidium, and cæsium tri-iodides. We may therefore ascribe the structural formula

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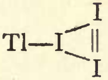
[1] V. Meyer, *Ber.*, 1879, **12**, 611 and 1199.

[2] Nilson and Pettersson, *Trans. Chem. Soc.*, 1888, **53**, 814; *Zeit. phys. Chem.*, 1888, **2**, 657.

[3] Maitland and Abegg, *Zeit. anorg. Chem.*, 1906, **49**, 341.



to thallium tri-iodide.

The trivalent nature of thallium is confirmed by preparation of its di-ethyl chloride derivative, $Tl(C_2H_5)_2 . Cl$, which is formed when zinc ethyl acts on thallium chloride. Double decomposition of this body with silver salts yields thallium di-ethyl salts. If the sulphate is prepared and decomposed with barium hydroxide, thallium di-ethyl hydroxide, $Tl(C_2H_5)_2 . OH$, is obtained which crystallizes from water in glistening needles, and exhibits a strongly alkaline reaction.

The recent researches of Denham,[1] seem to indicate that a subvalent thallium ion, $Tl_2^{\cdot}$, can exist in solution, and it is suggested that an explanation for the darkening action of light on the haloid salts must be sought for in this direction.

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[1] Denham, *Trans. Chem. Soc.*, 1908, **93**, 835.

XII

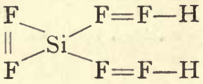
THE VALENCY OF THE ELEMENTS OF GROUP IV

To a consideration of the valency of the first element of this group, namely carbon, we have already devoted an entire chapter.[1]

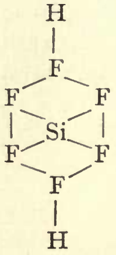
As early as 1863 Wöhler drew attention to the remarkable resemblances which exist between carbon and silicon. Of the tetravalent nature of the latter element there can be no reasonable cause for doubt. The hydride, SiH_4, and fluoride, SiF_4, have long been known.[2] The latter substance reacts with water, whereby silicic and hydrofluosilicic acids result,

$$3\,SiF_4 + 3\,H_2O = 2\,H_2SiF_6 + H_2SiO_3$$

In hydrofluosilicic acid, silicon appears at the first blush to be exerting eight valencies. It is more probable, however, that the fluorine is here trivalent. Thus:



or



where the atoms are arranged in a ring.

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[1] See Chapter VI.

[2] Gay Lussac and Thenard, *Gilbert's Ann.*, 1809, **32**, 1.

Silico-chloroform, $SiHCl_3$,[1] is obtained by the action of hydrochloric acid on copper silicide, and cooling the resulting products in liquid air. With ammonia, silicon nitrogen hydride, SiNH, is produced, the analogue of hydrocyanic acid, CNH.

Ruff and Albert[2] have further succeeded in preparing silico-fluoroform, $SiHF_3$, by the interaction of silico-chloroform and stannic fluoride. With alcohol, ethyl orthosilicate, $Si(OC_2H_5)_4$, is formed whilst with ether it yields ethyl orthosilico formate, $SiH(OC_2H_5)_3$.

Silicon tetra-iodide, SiI_4, and silico-iodoform, $SiHI_3$, are prepared by the action of iodine and hydriodic acid on heated silicon.[3] The bromo-iodide of silicon, $SiBr_3I$, boiling at 200°, is obtained by the action of bromine on silicon tetra-iodide.

The work of Friedel and Crafts[4] is interesting in this connection. These investigators have shown that when anhydrous alcohol is allowed to act on excess of silicon tetrachloride, a series of well-defined chlorohydrins is obtained. The composition and vapour densities of these bodies show that they are correctly represented by the formulæ

$$SiCl(OEt)_3, \quad SiCl_2(OEt)_2, \quad \text{and} \quad SiCl_3(OEt).$$

In all of these compounds silicon is clearly tetravalent. During the past few years the list of organic compounds of silicon has been largely increased by the researches of Ladenburg and others, and especially by those of Kipping and his co-workers.[5] The persistent efforts of Kipping to obtain optically active derivatives of silicon have at last been rewarded with success, and the analogy between this element and carbon is thus made complete.

With regard to titanium there is less to be said. The existence of such compounds as the hydride, TiH_4,[6] the tetrafluoride, TiF_4,[1] and the tetramide, $Ti(NH_2)_4$,[2] confirm the tetravalent nature of this element.

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[1] Friedel and Ladenburg, *Bull. Soc. chim.*, 1867, (2) **7**, 322; Ruff and Albert, *Ber.*, 1905, **38**, 2222.

[2] Ruff and Albert, *Ber.*, 1905, **38**, 53.

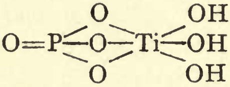
[3] Friedel, *Bull. Soc. chim.*, 1868, (2) **9**, 1.

[4] Friedel and Crafts, *Compt. rend.*, 1863, **56**, 324; **57**, 319.

[5] Kipping, *Trans. Chem. Soc.*, 1908, **93**, 457, 439, and 198; 1907, **91**, 726 and 209; 1901, **79**, 449.

[6] Renz, *Ber.*, 1906, **39**, 249.

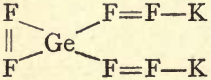
Faber[3] has recently discussed hexavalent titanium. A hexa-acetate is known, which is stable at low temperatures. It is yellow, and insoluble in acetic acid. On heating it exhibits a decidedly explosive character. A phosphate of hexavalent titanium is given the formula—



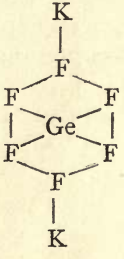
but this is open to criticism.

The next element, germanium, was discovered in 1886 by Winkler. Its existence had already been predicted by Mendeléeff in 1871, under the name of eka-silicon. Like silicon, germanium readily forms the tetra-ethyl compound $Ge(C_2H_5)_4$,[4] which is a liquid boiling at 160° C. This, together with the volatile tetrafluoride, GeF_4, suggests the tetravalency of the metal. In 1887, Nilson and Pettersson[5] showed from vapour density considerations that the formula to be attributed to germanium chloride is $GeCl_4$.

In view of these results it is more reasonable to assume that in K_2GeF_6, as in the analogous compound of silicon, we are dealing with trivalent fluorine. Thus:



or



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[1] Emrich, *Monatsh.*, 1904, **25**, 907; Ruff, Plato, and Graf, *Ber.*, 1904, **37**, 673.

[2] Stähler, *Ber.*, 1904, **37**, 4405; Stähler and Wirthwein, *Ber.*, 1905, **38**, 2619.

[3] Faber, *Zeit. anal. Chem.*, 1907, **46**, 277.

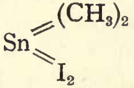
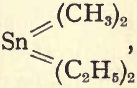
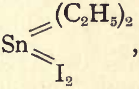
[4] Winkler, *J. pr. Chem.*, 1887, (2) **36**, 204.

[5] Nilson and Pettersson, *Zeit. phys. Chem.*, 1887, **1**, 27.

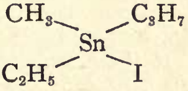
A similar explanation holds in the case of potassium fluostannate, K_2SnF_6,[1] since the tetravalency of tin is proved by the existence of such compounds as $SnCl_4$, $SnBr_4$,[2] SnF_4,[3] $Sn(C_2H_5)_4$,[4] and $Sn(C_6H_5)_4$.[5]

In stannous chloride, $SnCl_2$, tin functions as a divalent atom.[6] It is well known, however, that this salt forms an excellent reducer owing to its tendency to unite with more chlorine. Thus, mercuric chloride can by its agency be successively reduced to mercurous chloride and metallic mercury, according to the equations

$$2HgCl_2 + SnCl_2 = 2HgCl + SnCl_4$$
$$2HgCl + SnCl_2 = 2Hg + SnCl_4$$

Morgunoff[7] has shown that each pair of valencies of the tin atom is equivalent to the other. Thus, on treating the di-iododimethyl compound,  $\mathrm{Sn}{<}\begin{matrix}(CH_3)_2\\ I_2\end{matrix}$, with zinc di-ethyl, $Zn(C_2H_5)_2$, the same tetra-alkyl compound,  $\mathrm{Sn}{<}\begin{matrix}(CH_3)_2\\ (C_2H_5)_2\end{matrix}$, is obtained as by treating the di-iododi-ethyl compound,  $\mathrm{Sn}{<}\begin{matrix}(C_2H_5)_2\\ I_2\end{matrix}$, with zinc methyl, $Zn(CH_3)_2$.

In 1900, Pope and Peachey[8] succeeded in preparing an optically active tin derivative. Inactive methylethylpropyl stannic iodide,



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[1] See Kowalewsky, *Zeit. anorg. Chem.*, **25**, 189.

[2] Lorenz, *Zeit. anorg. Chem.*, **9**, 365; **10**, 44.

[3] Ruff, Plato, and Graf, *Ber.*, 1904, **37**, 673.

[4] Buckton, *Proc. Roy. Soc.*, 1859, **9**, 309.

[5] Polis, *Ber.*, 1889, **22**, 2917.

[6] Rieth, *Ber.*, 1870, **3**, 668.

[7] Morgunoff, *Annalen*, 1867, **144**, 157.

[8] Pope and Peachey, *Proc. Chem. Soc.*, 1900, **16**, 42 and 116.

was first isolated as a yellow oil, practically insoluble in water, and boiling at 270° C. Treatment with the requisite quantity of silver *d*-camphorsulphonate yielded an active crystalline salt, with $[M]_D = +9{\cdot}5°$. Pope and Neville,[1] therefore, suggest that the tetravalent tin atom resembles carbon in the arrangement of its valencies—a view in favour of which much may be said.

The existence of zirconium tetrafluoride, whose vapour density corresponds to the formula ZrF_4, proves the tetravalency of zirconium.[2]

Not less interesting is the behaviour of lead. This metal usually functions as a divalent atom. Thus, in qualitative analysis it is usually precipitated as the dichloride, $PbCl_2$, or as sulphide, PbS, and it is quantitatively estimated as sulphate, $PbSO_4$. Further, the isomorphism existing between the last-named salt and the sulphates of barium and strontium confirms the divalent nature of lead. Also, F. M. Perkin[3] has recently prepared lead ethoxide, $Pb(OC_2H_5)_2$, by the action of ozone and absolute alcohol on thin lead sheets.

Nevertheless, a considerable body of evidence has been collected to show that lead may also be tetravalent, and this justifies its inclusion in the present group.

In 1893, Friedrichs[4] prepared the tetrachloride, $PbCl_4$, and Hutchinson and Pollard[5] isolated the tetra-acetate and tetrapropionate.

The most convincing proof, however, lies in the preparation of lead tetra-ethyl, $Pb(C_2H_5)_4$,[6] and lead tetraphenyl,[7] $Pb(C_6H_5)_4$. This last-named body is readily obtained by mixing Grigniard's reagent, $C_6H_5 . Mg . Br$, with lead dichloride at ordinary temperatures. Thus:

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[1] Pope and Neville, *Trans. Chem. Soc.*, 1902, **81**, 1552.

[2] Wolter, *Chem. Zeit.*, 1908, **32**, 606; compare Marignac, *Jahresber.*, 1860, p. 136.

[3] Perkin, *Proc. Chem. Soc.*, 1908, **24**, 179.

[4] Friedrichs, *Ber.*, 1893, **26**, 434.

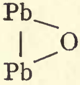
[5] Hutchinson and Pollard, *Trans. Chem. Soc.*, 1893, **63**, 1136.

[6] Ghira, *Atti Roy. Acad. Lincei*, 1893, (5) **2**, ii, 216; Buckton, *Proc. Roy. Soc.*, 1859, **9**, 309.

[7] Michaelis and Polis, *Ber.*, 1887, **20**, 716 and 331; Pfeiffer and Truskier, *Ber.*, 1904, **37**, 1125.

$$2PbCl_2 + 4C_6H_5MgBr = Pb + Pb(C_6H_5)_4 + 2MgCl_2 + 2MgBr_2$$

Recent research points very clearly to the fact that lead can function as a monovalent atom also. The existence of lead suboxide, Pb_2O, has been rendered tolerably certain by the experiments of Tanatar.[1] This body, of course, might be represented by the formula



in which the lead is clearly divalent (compare cadmium). Brislee[2] has also been led to believe that lead can function as a monovalent atom by a study of the reduction of lead oxide by carbon monoxide. The experiments of Denham and Allmand[3] lend further support to this view. It would seem, therefore, that the power of lead to function as a mono-, di-, and tetra-valent element has been demonstrated.

The tetravalency of the last element of this group, namely thorium, is proved by the results of vapour density determinations of the tetrachloride,[4] which show that its formula is $ThCl_4$. The hydride, ThH_4, has also been isolated.

The element cerium was originally placed in this group by Mendeléeff, on account of its tendency to form tetravalent derivatives. The correctness of this procedure has been called into question by several chemists, who argue that cerium more properly belongs to the third group, along with aluminium and gallium, owing to the greater stability manifested by the cerous salts. Barbieri[5] points out, however, that it is not strictly accurate to say that the cerous salts are stable, and that the ceric salts are not. It is really the ion $Ce^{\cdot\cdot\cdot\cdot}$ which is unstable, being readily transformed into the ion $Ce^{\cdot\cdot\cdot}$. It appears that, in alkaline solution, in which ceric ions cannot exist, ceric compounds are stable, whereas cerous compounds act as reducing agents. At present, therefore, there can be no reasonable doubt that cerium properly belongs to the fourth group in the Periodic Table.[1]

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[1] Tanatar, *Zeit. anorg. Chem.*, 1901, **27**, 304.

[2] Brislee, *Trans. Chem. Soc.*, 1908, **93**, 154.

[3] Denham and Allmand, *Trans. Chem. Soc.*, 1908, **93**, 425; Denham, *Trans. Chem. Soc.*, 1908, **93**, 834.

[4] Krüss and Nilson, *Ber.*, 1887, **20**, 1665; Troost, *Compt. rend.*, 1885, **101**, 360.

[5] Barbieri, *Atti R. Accad. Lincei*, 1907, (v.) **16**, i., pp. 395, 525 and 644.

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[1] See also Morgan and Cahen, *Trans. Chem. Soc.*, 1907, **91**, 475; Wolff, *Zeit. anorg. Chem.*, 1905, **45**, 89.

XIII

THE VALENCY OF NITROGEN

THE study of the valency of nitrogen is one of particular interest and importance. One might imagine that such an inactive gas as nitrogen is, in its behaviour towards oxygen, hydrogen, and chlorine, would be incapable of forming stable compounds with other elements; in other words, that its valencies would be exceedingly weak. This, however, is not the case.

The simplest hydride of nitrogen is ammonia, NH_3, in which nitrogen functions as a trivalent atom. No other hydride is known containing more than three atoms of hydrogen for every atom of nitrogen. Kekulé, therefore, assumed that this element was trivalent.

In ammonium chloride, however, the atom of nitrogen is apparently pentavalent. Kekulé argued that this salt is really a molecular compound, the formula for which would be more correctly written as $NH_3 . HCl$. Deville and Troost[1] showed in 1862 that its vapour density was approximately half that required by theory, and Pebal[2] and Than[3] proved that this was caused by its dissociation into ammonia and hydrochloric acid. In this way Kekulé's view was apparently proved to be correct. Deville considered that the dissociation was the result of contact action between the vaporized salt and the asbestos used in the experiment. Than showed, however, that when a porous diaphragm was substituted for asbestos, dissociation still took place. He further drew attention to the

[1] Deville and Troost, *Annalen*, 1862, **123**, 199.

[2] Pebal, *Annalen*, 1862, **123**, 193.

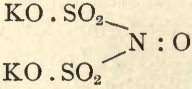
[3] Than, *Annalen*, 1864, **131**, 138.

fact that when the two gases, ammonia and hydrochloric acid, were mixed at 350° C., no contraction or expansion took place. This, at the first blush, seems to be in direct antagonism to the results obtained by Deville, who caused the two gases to mix in a vessel heated by the vapour of boiling mercury, and observed a rise of temperature. But, as Ramsay and Young[1] have shown, the vapour density of ammonium chloride varies with the pressure as well as the temperature. Consequently the experiments of Deville and Than are not comparable.

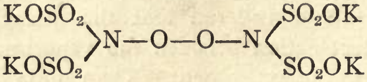
In a series of remarkable investigations, Baker[2] has shown that ammonium chloride, when perfectly dry, may be vaporized without dissociating, a result which F. Johnson[3] has recently confirmed. This establishes the pentavalency of nitrogen.

In nitric oxide, NO, whose molecules are single at temperatures as low as −100° C., the valency of nitrogen evidently depends on that of oxygen. As we shall see in a later chapter, oxygen can function as a tetravalent atom, and in Chapter XIX. reasons are adduced to show that in nitric oxide we have **the first example of tetravalent nitrogen.** All efforts to obtain other derivatives of tetravalent nitrogen have, up to the present, resulted in failure.

In 1906, Raschig[4] believed that the potassium salt of peroxylaminesulphonic acid



was the first definitely established example of tetravalent nitrogen. Haga, however, doubles the formula, thus:[5]



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[1] Ramsay and Young, *Phil. Trans.*, 1886, **177**, (1) 99.

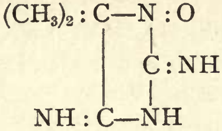
[2] Baker, *Trans. Chem. Soc.*, 1894, **65**, 612.

[3] F. Johnson, *Zeit. phys. Chem.*, 1908, **61**, 457.

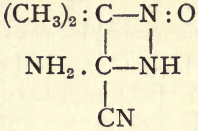
[4] Raschig, *Ber.*, 1906, **39**, 246.

[5] Haga, *Trans. Chem. Soc.*, 1904, **85**, 78.

Piloty and Schwerin,[1] give as the formula of porphyrexide the alternative schemes—



and



in which tetravalent nitrogen is present in the form of $=N:O$. So far as the present author is aware, these results have not received confirmation.

When sodium amalgam is thrown into a solution of ammonium chloride, the sodium dissolves, and the mercury swells up to an enormous spongy mass. After a few minutes, during which ammonia and hydrogen gas are evolved, the mercury contracts and regains its original volume. This spongy mass is frequently spoken of as ammonium amalgam, and by many it is supposed to be a solution of ammonium, NH_4, in mercury. The equation representing the change may be expressed as follows:

$$HgNa_2 + 2NH_4Cl = Hg(NH_4)_2 + 2NaCl$$

where, for the sake of simplicity, it is assumed that sodium and ammonium amalgams have the general formula HgM_2.

It is found, however, that the sponge-like mass, when subjected to changes of pressure, contracts and expands in conformity to Boyle's Law. Many chemists therefore believe that it is simply a solution of ammonia and hydrogen gases in mercury, and no amalgam at all. A decisive solution of the problem has yet to be found.[2]

Werner writes the formula for ammonium chloride as

$$H_3N \ldots HCl$$

where the dotted line indicates an auxiliary valence. Here the nitrogen is represented as tetravalent. There are, however, several objections to this formula, as we shall see in a later chapter.[1]

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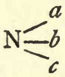
[1] Piloty and Schwerin, *Ber.*, 1901, **34**, 1884 and 2354.

[2] See, Le Blanc, *Zeit. phys. Chem.*, 1890, **5**, 467; Pocklington, *Zeit. Electro-chemie*, 1899, **5**, 139; Coehn, *Zeit. anorg. Chem.*, 1900, **25**, 425; Ruff, *Ber.*, 1901, **34**, 2604; Rich and Travers, *Trans. Chem. Soc.*, 1906, **89**, 872; Travers, *Ber.*, 1907, **40**, 3949; Smith, *ibid.*, pp. 2941, 4298, and 4893; Franklin, *J. Amer. Chem. Soc.*, 1907, **29**, 35; Moissan, *Compt. rend.*, 1907, **144**, 790.

In such complexes as NH_4I_3,[2] $N(CH_3)_4I_5$,[3] $C_5H_5NIClHCl$,[4] $C_6H_5(CH_3)_2 . C_2H_5 . NCl . ICl_3$.[5] and others of a similar nature, nitrogen might appear to have a valency varying from five to nine. It is more reasonable to suppose, however, that nitrogen is but pentavalent, and that the iodine and chlorine have, in these cases, a greater valency than unity. From the foregoing it is clear that the valency of nitrogen varies from three to five. And only in very exceptional cases does it appear to be four.

We have every reason to believe that the three valencies of trivalent nitrogen lie in one plane, since all attempts to prepare optically active derivatives of the type



have failed.[6]

On the other hand, active derivatives of pentavalent nitrogen have been prepared. Thus Le Bel[7] in 1891 was able to discover a slight activity by allowing mould to act on dilute solutions of methylethylpropyl*iso*butylammonium chloride. Since then many other active compounds of pentavalent nitrogen have been prepared, a fact which apparently proves that the fourth and fifth valencies of the nitrogen atom lie in a different plane from the other three.[1]

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[1] See Chapter XVIII.

[2] Abegg and Hamburger, *Zeit. anorg. Chem.*, 1906, **50**, 403.

[3] Weltzien, *Annalen*, 1854, **91**, 41.

[4] Ostermeyer, *Chem. Zentr.*, 1884, **15**, 939.

[5] E. A. Werner, *Trans. Chem. Soc.*, 1906, **89**, 1630.

[6] See, V. Meyer, *Ber.*, 1890, **23**, 567; Krafft, *Ber.*, 1890, **23**, 2780; Behrend and König, *Annalen*, 1891, **263**, 175; Ladenburg, *Ber.*, 1893, **26**, 864; Fischer, *Ber.*, 1899, **32**, 2470; Reychler, *Bull. Soc. chim.*, 1902, (3) **27**, 979; Jones and Millington, *Proc. Camb. Phil. Soc.*, 1904, **85**, 438; Kipping and Salway, *Trans. Chem. Soc.*, 1904, **85**, 438.

[7] Le Bel, *Compt. rend.*, 1891, **112**, 724. See also Le Bel, *Comp. rend.*, 1904, **129**, 548; Pope and Peachey, *Trans. Chem. Soc.*, 1899, **75**, 1127; Pope and Harvey, *ibid.*, 1901, **79**, 828; Jones, *ibid.*, 1903, **83**, 1418; 1904, **85**, 223; 1905, **87**, 135; Wedekind, *Ber.*, 1904, **37**, 2727; Thomas and Jones, *Trans. Chem. Soc.*, 1906, **89**, 280; Frölich, *Ber.*, 1906, **39**, 4437.

On mathematical grounds it is clear that if the five valencies of nitrogen do not lie in one plane, they cannot all be similar. If we imagine that the five radicles attached to the nitrogen lie on a sphere, two courses are open to us. We may assume that the positions are interchangeable, in which case no isomerism of the type $NR_2R'_2Cl$ becomes possible. On the other hand, if the positions are regarded as fixed and invariable, we should expect isomers to be formed.

In order to settle this question, Victor Meyer and Lecco,[2] studied the mixed methylethylammonium derivatives. They found that the same compound was formed by acting on dimethylamine with ethyl iodide

$$(CH_3)_2NH + 2C_2H_5I = (CH_3)_2N(C_2H_5)_2I + HI$$

as by the action of di-ethylamine on methyl iodide,

$$(C_2H_5)_2NH + 2CH_3I = (C_2H_5)_2N(CH_3)_2I + HI$$

This result is usually accepted as a proof that ammonium compounds are atomic combinations, and not mere molecular associations as Kekulé suggested. Further, the equivalence of four of the valencies of the nitrogen atom is regarded as demonstrated, namely those by which the alkyl groups are attached.

Lossen,[3] however, very correctly draws attention to the fact that these results are not necessarily conclusive, but will bear another interpretation. It is quite possible, he argues, that during the reaction the groups undergo rearrangement to a favoured position, and hence the same compound always results. He further points out that no arguments based on crystalline structure are conclusive, for there is no reason why two isomers represented by the formulæ

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[1] It is not necessary to give in detail the experimental work, as this would be beyond the scope of the present volume. A very excellent summary will be found in Dr. Stewart's book, entitled *Stereochemistry* (this series), Longmans and Co., 1907.

[2] V. Meyer and Lecco, *Annalen*, 1876, **180**, 173; *Ber.*, 1876, **8**, 233.

[3] Lossen, *Annalen*, 1876, **181**, 364.

$$(CH_3)_2N(C_2H_5)_2I \quad \text{and} \quad (C_2H_5)_2N(CH_3)_2I$$

respectively, should not be isomorphous. If, now, we assume that isomerism is impossible when the radicles attached to the nitrogen are light, owing to the interchangeability of their positions, yet it is quite possible for isomerism to occur when heavy radicles are introduced into the molecule, for then the positions might less easily be interchanged.

Wedekind[1] was of the opinion that isomeric forms of phenylbenzylmethylallyl ammonium iodide were obtained when allyl iodide was allowed to interact with benzylmethyl aniline, and methyl iodide with benzylallylaniline. Jones[2] has shown, however, that the supposed isomeride from the latter reaction is in reality phenylbenzyldimethylammonium iodide.

Le Bel[3] examined a whole series of mixed ammonium platinic chlorides belonging to the cubic system, in order to determine the stages at which the cubic symmetry vanishes. He found that whilst trimethylpropylammoniumplatinichloride was cubic, the *iso*butyl compound was dimorphous. The question is, Are these derivatives isomers, or simply cases of dimorphism, such as that exhibited by calcium carbonate? Le Bel[4] is now inclined to the latter view.

Schryver[5] has extended Le Bel's work by showing that two platinum salts of methyldi-ethyl*iso*amylammonium chloride can be isolated. Ladenburg[6] made a study of the benzyl ethyl ammonium derivatives, and showed that the body obtained by the action of benzyl chloride on tri-ethylamine, and subsequent replacement of the chlorine by iodine

$$(C_2H_5)_2N(C_2H_5) + C_6H_5 . CH_2Cl \longrightarrow (C_2H_5)_2N(C_2H_5)(C_6H_5 . CH_2)I$$

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[1] Wedekind, *Ber.*, 1899, **32**, 517.

[2] Jones, *Trans. Chem. Soc.*, 1905, **87**, 1721.

[3] Le Bel, *Compt. rend.*, 1890, **110**, 145; 1893, **116**, 513.

[4] Le Bel, *J. Chim. Phys.*, 1904, **2**, 340.

[5] Schryver, *Proc. Chem. Soc.*, 1891, **7**, 39.

[6] Ladenburg, *Ber.*, 1887, **10**, 43 and 1634.

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is not identical with that produced by the combination of ethyl iodide and di-ethylbenzylamine

$$(C_6H_5 . CH_2)(C_2H_5)N(C_2H_5) + C_2H_5I \longrightarrow (C_6H_5 . CH_2)(C_2H_5)N(C_2H_5)_2I$$

For the former body on treatment with hydriodic acid readily parts with benzyl iodide. Not so the latter.

It is not impossible, therefore, that when benzyl chloride acts on tri-ethylamine, the complex

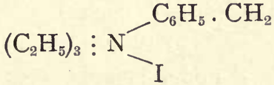
$$(C_2H_5)_3N{=}Cl(C_6H_5 . CH_2)$$

is obtained, analogous to $H_3N{=}ClH$ to which attention is directed in a later chapter.[1] The iodine compound derived from it will therefore have a similar structure, namely

$$(C_2H_5)_3N{=}I(C_6H_5 . CH_2)$$

The existence of these two isomers may therefore be regarded as evidence in favour of the assumption that in many cases, particularly with chlorine, when additions are made to trivalent nitrogen, so-called molecular compounds are first formed, which then may or may not undergo rearrangement to atomic compounds.

The second of Ladenburg's compounds will evidently have the formula



$$(C_2H_5)_3 : N\begin{matrix} \diagup C_6H_5 . CH_2 \\ \diagdown I \end{matrix}$$

In order to explain the differences between the fourth and fifth valencies, van't Hoff[2] supposes that the nitrogen atom lies inside a cube, towards five corners of which its valencies are directed. It is clear that by suitably choosing the position of the point representing the nitrogen atom, three of the valencies may be made equal in value, the remaining two being different both from themselves and from the other two.

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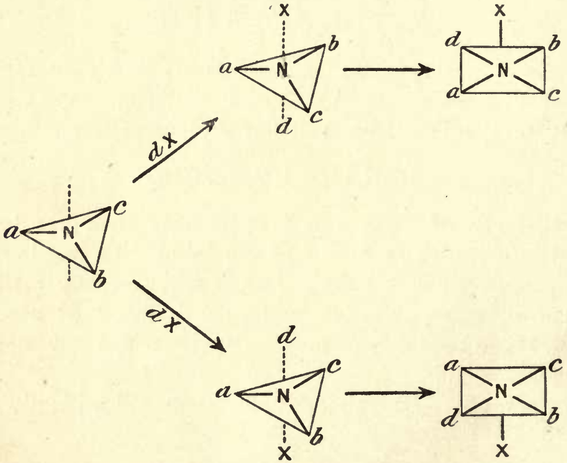
[1] See Chapter XIX.

[2] Van't Hoff, *Ansichten über die organische Chemie*, p. 79.

Willgerodt,[1] Burch and Marsh,[2] Behrend,[3] and Béhal[4] have suggested somewhat similar ideas.

The views of H. O. Jones[5] are of interest since they are based on stereochemical considerations. Jones takes exception to van't Hoff's representation of the fourth and fifth valencies, on the ground that if one of the valencies were predestined to become attached to an alkyl group, and the other to the negative radicle, then only *one* of the two optical isomers known could be produced. This, however, is contrary to experience, for the *d* and *l* isomers are produced in equal quantities. Since the three valencies of trivalent nitrogen, as we have already seen, lie in one plane, Jones assumes that on calling out the two other valencies, a definite rearrangement in space takes place whereby two compounds are formed, related to one another as the object to its mirror image. This is well illustrated by Fig. 2.



(*From Stewart's "Stereochemistry."*)

FIG. 2.

Another suggestion is considered in Chapter XIX.

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[1] Willgerodt, *J. pr. Chem.*, 1888, (2) **37**, 450; 1890, (2) **41**, 291.

[2] Burch and Marsh, *Trans. Chem. Soc.*, 1889, **55**, 656.

[3] Behrend, *Ber.*, 1890, **23**, 454.

[4] Béhal, *Conférences de la Chimie*, 1896, **4**, 60.

[5] Jones, *Trans. Chem. Soc.*, 1903, **83**, 1403; 1905, **87**, 1721.

XIV

THE VALENCY OF THE ELEMENTS OF GROUP V

THE valency of nitrogen, the first member of this group, has already received full consideration.

In the hydride, PH_3, phosphorus is clearly trivalent, and all efforts to isolate phosphonium, PH_4, have proved unavailing. In phosphorus pentachloride, PCl_5, we have a dissociable substance, and one which Kekulé classed as a molecular compound, $PCl_3 . Cl_2$. Wurtz[1] has shown, however, that in the presence of excess of trichloride, the pentachloride can be vaporized without decomposition. Further, the experiments of Baker[2] indicate that, if the perfectly dry pentachloride could be obtained and vaporized under ordinary conditions, the amount of dissociation would be inappreciable. This throws considerable doubt on the correctness of Kekulé's formula. In 1876, Thorpe[3] confirmed the pentavalency of phosphorus by preparing the pentafluoride, PF_5, which can exist in the gaseous state without decomposition. The variability of the valency of phosphorus is well illustrated by the two isomeric compounds of the formula $PO(C_6H_5)_3$.[4] The one is a thick, oily liquid, prepared by the action of diphenylchlorophosphine upon phenol

$$(C_6H_5)_2PCl + C_6H_5OH = (C_6H_5)_2 : P . O . C_6H_5 + HCl$$

whereas the second isomer is solid, melting at 153·5° C., and is prepared by the interaction of triphenylbromophosphine bromide and water

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[1] Wurtz, *Compt. rend.*, 1873, **76**, 601.

[2] Baker, *Trans. Chem. Soc.*, 1900, **77**, 646.

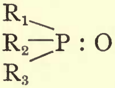
[3] Thorpe, *Annalen*, 1876, **182**, 201.

[4] See Michaelis and La Coste, *Ber.*, 1885, **18**, 2118.

$$(C_6H_5)_3PBr_2 + HOH = (C_6H_5)_3 \vdots P : O + 2HBr$$

In the former case the phosphorus is clearly trivalent, whereas in the latter it is undoubtedly pentavalent. In PCl_6I,[1] and PCl_3Br_4,[2] phosphorus might appear to be heptavalent, and in PCl_3Br_8[3] its valency is apparently eleven. As in the analogous derivatives of nitrogen, it is perhaps more reasonable to assume that the valencies of the halogens are in these cases greater than unity, whilst the valency of phosphorus does not exceed five.

Caven[4] has shown that the three valencies of trivalent phosphorus probably lie in one plane, as is the case for nitrogen. We should therefore expect



to yield active salts; but this expectation has not been realized. Michaelis[5] was unable to obtain activity with compounds of the type P*abcd*X, but it is quite possible that this was due to the poisonous action of these substances upon the ferments employed.

Judging from its hydride, AsH_3, we should be led to attribute to arsenic a valency of three, as in the case of nitrogen. Such an assumption receives support from the work of Smith and Hora.[6] These investigators have studied the cryoscopy of the solution of chlorine in arsenic trichloride, and conclude that no pentachloride is formed.

When gaseous ammonia is allowed to act on arsenic

[1] Bandrimont, *Jahresber.*, 1862, p. 54.

[2] Michaelis, *Ber.*, 1872, **5**, 411.

[3] Prinvault, *Compt. rend.*, 1872, **74**, 868; Michaelis, *op. cit.*, p. 415.

[4] Caven, *Trans. Chem. Soc.*, 1902, **81**, 1362.

[5] Michaelis, *Annalen*, 1901, **315**, 58.

[6] Smith and Hora, *J. Amer. Chem. Soc.*, 1904, **26**, 632.

trichloride at low temperatures, arsenamide, $As(NH_2)_3$, is produced.

$$AsCl_3 + 3\,NH_3 = 3\,HCl + As(NH_2)_3$$

This, at 250°, yields arsenic nitride, AsN, in which arsenic has a valency of three or five, according as we regard nitrogen as tri- or penta-valent.[1]

In 1906, Ruff and Graf[2] succeeded in preparing arsenic pentafluoride, in which the valency of arsenic is clearly five. The numerous alkyl derivatives[3] further support its tri- and penta-valency. This is well illustrated by the chloro-alkyl derivatives[4] of pentavalent arsenic, which, on being heated, lose a molecule of the alkyl chloride, and leave a residue containing trivalent arsenic. Thus, $As(CH_3)Cl_4$ breaks down at 0° C., and $As(CH_3)_2Cl_3$ at 50° C. The equations representing these changes are as follows—

$$\begin{aligned} As(CH_3)_3Cl_2 &\longrightarrow As(CH_3)_2Cl + CH_3Cl \\ As(CH_3)_2Cl_3 &\longrightarrow As(CH_3)Cl_2 + CH_3Cl \\ As(CH_3)Cl_4 &\longrightarrow AsCl_3 \qquad\quad + CH_3Cl \end{aligned}$$

The resemblance between antimony and arsenic is very close. Antimony forms a trihydride, SbH_3, and a pentafluoride.[5] In contradistinction to arsenic it forms a pentachloride, and the oxychlorides $SbOCl_3$ and SbO_2Cl are well known. The derivatives of the pentafluoride have been carefully studied by Ruff and his co-workers.[6] Whilst chlorine has no action, bromine forms a viscid, dark brown mass, to which the formula SbF_5Br is given. With iodine two compounds are formed, namely $(SbF_5)_2I$ and SbF_5I, whilst with sulphur a hygroscopic substance, SbF_5S, is obtained. The formation of these bodies may be explained in two ways, (1) by attributing to antimony a greater valency than five, (2) by assuming that fluorine is not strictly monovalent, and that the bromine, iodine, and sulphur are attached directly to it, and not to the antimony. This latter explanation is most probably correct. No evidence has been obtained of the existence of a fluoride of chlorine, although Lebeau[1] has brought these elements together at very low temperatures. This would explain why chlorine is without action on the pentafluoride. Bromine, iodine, and sulphur, on the other hand, form very definite compounds with fluorine. Thus bromine yields a trifluoride, BrF_3,[2] iodine a pentafluoride, IF_5,[3] and sulphur a hexafluoride.[4]

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[1] Hugot, *Compt. rend.*, 1904, **139**, 54.

[2] Ruff and Graf, *Ber.*, 1906, **39**, 67.

[3] See Bunsen, *Annalen*, 1841, **37**, 1; 1842, **42**, 14; 1843, **46**, 1; Cahours and Riche, *Annalen*, 1854, **92**, 361; Landolt, *Annalen*, 1854, **92**, 370; Michaelis, *Ber.*, 1875, **8**, 1316.

[4] See Baeyer, *Annalen*, 1858, **107**, 257.

[5] Ruff and Plato, *Ber.*, 1904, **37**, 673.

[6] Ruff, Heller, Knock, and Graf, *Ber.*, 1906, **39**, 4310.

It is not surprising, therefore, that these elements unite with antimony pentafluoride.

The organic derivatives of antimony are less important than those of arsenic, nevertheless those which have been studied point conclusively to the power of antimony to act both as a tri- and penta-valent atom.

Trimethyl stibine, $Sb(CH_3)_3$, and tri-ethyl stibine, $Sb(C_2H_5)_3$, are liquids, which combine energetically with the chlorine of concentrated hydrochloric acid, whereby a derivative of pentavalent antimony results. Thus:

$$Sb(C_2H_5)_3 + 2HCl = Sb(C_2H_5)_3Cl_2 + H_2$$

Pentamethyl stibine, $Sb(CH_3)_5$, and penta-ethyl stibine, $Sb(C_2H_5)_5$, are also known.

It would seem as if antimony were tetravalent in such compounds as Rb_2SbCl_6,[5] (compare K_2SiF_6).

The remaining element, bismuth, presents many points of interest. As a rule it functions as a trivalent atom. Thus, for example, its compounds with the halogens have the general formula BiX_3.

Bismuth trimethyl, $Bi(CH_3)_3$, and tri-ethyl, $Bi(C_2H_5)_3$, have both been prepared.[1] The former yields the trichloride with hydrochloric acid. The latter, with iodine, yields bismuth diethyl iodide, $Bi(C_2H_5)_2I$, whilst treatment with mercuric chloride results in the formation of bismuth ethyl chloride, $Bi(C_2H_5)Cl_2$, according to the equation

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[1] Lebeau, *Compt. rend.*, 1906, **143**, 425.

[2] Prideaux, *Proc. Chem. Soc.*, 1905, **21**, 240.

[3] Gore, *Chem. News*, 1871, **24**, 291.

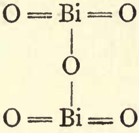
[4] Moissan and Lebeau, *Compt. rend.*, 1900, **130**, 865.

[5] Weinland and Schmid, *Ber.*, 1905, **38**, 1080.

$$Bi(C_2H_5)_3 + 2HgCl_2 = Bi(C_2H_5)Cl_2 + 2Hg(C_2H_5)Cl$$

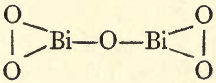
Bismuth triphenyl, $Bi(C_6H_5)_3$, is also known.[2]

In bismuth pentoxide, Bi_2O_5, we might assume a pentavalent atom, and write the formula graphically as follows:



$$\begin{array}{c} O = Bi = O \\ | \\ O \\ | \\ O = Bi = O \end{array}$$

Of course we have no proof that this is correct, and we might perhaps with equal reason write the formula



in which bismuth remains trivalent. This peroxide formula would afford an explanation for the ease with which the oxygen is evolved, both on heating and on treatment with acids. On the other hand, the existence of such complexes as $(CH_3)_3BiBr_2$, $(C_6H_5)_3BiCl_2$, and $(C_6H_5)_3BiBr_2$,[3] points clearly to the pentavalency of the metal.

It seems impossible to prepare a pentachloride of bismuth,[4] and bismuth trifluoride does not combine directly with fluorine. Nevertheless Ruff[5] and his co-workers have recently obtained evidence to show that traces of a higher fluoride are formed by the action of fluorine on bismuth trifluoride at −80° C. When bismuthic acid is added to concentrated hydrofluoric acid, a colourless, very unstable solution of bismuth oxytrifluoride, $BiOF_3$, is obtained, in which bismuth is clearly pentavalent.

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[1] Marquardt, *Ber.*, 1887, **20**, 1516; 1888, **21**, 2035.

[2] Michaelis and Marquardt, *Annalen*, 1889, **251**, 324.

[3] Michaelis, *Ber.*, 1887, **20**, 52; Gillmeister, *Ber.*, 1897, **30**, 2843.

[4] Hutchins and Lenher, *J. Amer. Chem. Soc.*, 1907, **29**, 31.

[5] Ruff, Knoch, and Zedner, *Zeit. anorg. Chem.*, 1908, **57**, 220.

It is not often that bismuth is regarded as a divalent element. Berthelot[1] in 1828 claimed to have prepared a derivative of divalent bismuth, as did Heinz,[2] Weber,[3] and Schneider[4] some years later. The subject was again revived by Tanatar[5] in 1901, who prepared bismuth suboxide, BiO, by heating the basic oxalate, $Bi_2O_2 . C_2O_4$, which decomposes completely into BiO and carbon dioxide.

Brislee[6] has studied the rate of reduction of bismuth oxide in carbon monoxide and finds that the time-reduction curve shows a break very close to the point of completion of this reaction[7]

$$Bi_2O_3 \longrightarrow 2BiO$$

Denham[8] has obtained further evidence of the existence of divalent bismuth.

Herz and Guttmann[9] have studied the freezing-point curve of the system bismuth trichloride—bismuth. The curve shows a maximum corresponding with the composition of bismuthous chloride, $BiCl_2$, and the formation of this compound is confirmed by the fact that its density is lower than that of a mixture of bismuth trichloride and bismuth of corresponding composition. Bismuthous bromide and iodide have also been prepared. It would appear, therefore, that bismuth is capable of functioning as a di-, tri-, and penta-valent atom.

[1] Berthelot, *J. Pharm.*, 1828, **14**, 616.

[2] Heinz, *Pogg. Ann.*, 1844, **63**, 55.

[3] Weber, *ibid.*, 1859, **107**, 596.

[4] Schneider, *ibid.*, 1855, **96**, 130.

[5] Tanatar, *Zeit. anorg. Chem.*, 1901, **27**, 437.

[6] Brislee, *Trans. Chem. Soc.*, 1908, **93**, 163.

[7] See Herz and Guttmann, *Zeit. anorg. Chem.*, 1907, **53**, 63.

[8] Denham, *Trans. Chem. Soc.*, 1908, **93**, 833.

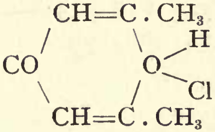
[9] Herz and Guttmann, *Zeit. anorg. Chem.*, 1908, **56**, 422

XV

THE VALENCY OF THE ELEMENTS OF GROUP VI

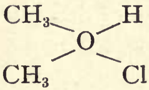
UNTIL comparatively recently oxygen was regarded as a splendid example of a divalent element of invariable valency. Thus, in water, chlorine monoxide, and a host of other substances, it would be difficult to attribute to oxygen a higher valency than two.

In 1899, Collie and Tickle[1] pointed out that oxygen could function as a tetravalent atom. They studied the hydrochloride of dimethylpyrone, and gave it the formula



The list of compounds containing tetravalent oxygen was rapidly increased by the investigations of Kehrmann,[2] Willstätter and Iglauer,[3] Bülow and Sicherer,[4] Baeyer and Villiger,[5] and others.

Friedel[6] found that methyl ether combines with hydrochloric acid to give an oxonium salt, whose constitution is usually given as



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[1] Collie and Tickle, *Trans. Chem. Soc.*, 1899, **75**, 710.

[2] Kehrmann, *Ber.*, 1899, **22**, 2601.

[3] Willstätter and Iglauer, *Ber.*, 1900, **33**, 1636.

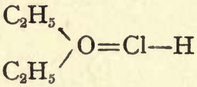
[4] Bülow and Sicherer, *Ber.*, 1901, **34**, 3916.

[5] Baeyer and Villiger, *Ber.*, 1901, **34**, 2685.

[6] Friedel, *Bull. Soc. chim.*, 1875, (ii.) **24**, 160 and 241.

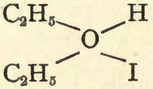
This structural formula shows perfect analogy with the ammonium compounds, and the term oxonium, as applied to these salts, receives, therefore, full justification.

There is a second way, however, in which the above compound may be represented. Bearing in mind the fact that hydrochloric acid is a very stable compound, and that the oxonium salt is easily dissociable, it seems most probable that the complex

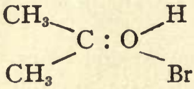


is first formed. A portion of this then undergoes rearrangement until equilibrium is obtained between the two tautomers, much in the same way as occurs in the case of the enolic and ketonic forms of acetacetic ester.

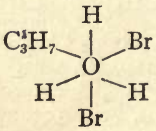
Archibald and McIntosh[1] have studied the compounds formed by liquid halogen hydrides and organic bodies such as acetone and ether. It is suggested that the compound $(C_2H_5)_2O$. HI has the constitution



and that $(CH_3)_2CO$. HBr is



The assumption is also made that the valency of oxygen increases as the temperature decreases. Thus, the compound C_3H_7OH . 2HBr is represented as



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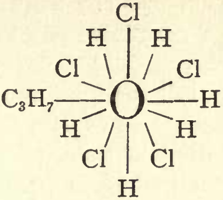
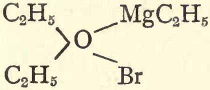
[1] Archibald and McIntosh, *Trans. Chem. Soc.*, 1904, **85**, 919.

in which oxygen is hexavalent, and $C_3H_7OH . 5 HCl$ as

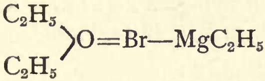


where oxygen is given a valency of twelve.[1] This, however, is very unlikely. It is far more reasonable to suppose that the halogens are here trivalent, and oxygen not more than tetravalent.

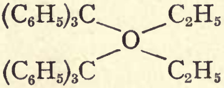
When magnesium filings are added to alkylogens dissolved in ether, heat is set free, and an alkyl group, together with one atom of the halogen, unites with the metal, whereby the complex $BrMgC_2H_5$ is formed. This combines, however, with a molecule of ether to yield an oxonium derivative, to which the formula



is usually ascribed.[2] It is not impossible, however, that the bromine is here trivalent, thus:



Triphenylmethyl, discovered by Gomberg[3] in 1900, and to which the formula $C(C_6H_5)_3$ has been temporarily assigned, unites with ether to form a derivative of tetravalent oxygen, namely,



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[1] See McIntosh, *Trans. Chem. Soc.*, 1905, **87**, 784; *J. Amer. Chem. Soc.*, 1905, **27**, 1013; 1906, **28**, 588; Walker, McIntosh and Archibald, *Trans. Chem. Soc.*, 1904, **85**, 1098.

[2] Pfeiffer and Truskier, *Ber.*, 1904, **37**, 1125.

[3] See p. 42, for references.

If it were possible to cause four different groups to attach themselves to the oxygen, optically active compounds might result. This would be a conclusive proof of the tetravalency of oxygen.

Bülow and Sicherer[1] call the third and fourth valencies of the oxygen *crypto-valencies*, and explain the tendency of the oxygen to revert to the divalent state, by the assumption that these valencies can be absorbed in much the same way as Thiele's partial valencies are absorbed in certain circumstances.

Baeyer and Villiger[2] are inclined to dispute the correctness of the term *oxonium salts* as applied to these compounds. They regard them as complex bodies formed by the oxygen exhibiting two ordinary valencies and a *complex valence*. According to Werner, the platinum atom contains four ordinary, and two auxiliary valencies. Thus:

$$Cl_4\equiv Pt :::: (HCl)_2$$

The oxygen atom therefore resembles a half-platinum atom, thus:

$$C{=}O\,..\,(HCl)$$

We have evidence to show that liquid water is associated, although to what extent is not definitely known, for all the methods which have been employed to determine its association are open to criticism.[3] If the molecules are double, the formula is clearly

$$H_2{=}O{=}O{=}H_2$$

If of a higher order, the oxygen atoms are presumably arranged in a ring.

In 1890, Beckmann[4] pointed out that all associated liquids are of the water type, and it is now a well-recognized fact, that substances containing hydroxyl groups usually form associated molecules when in the liquid condition.[1] Ramsay and Shields examined a number of alcohols and fatty acids, and found that these were always associated. Auwers and his co-workers[2] have cryoscopically investigated the molecular weights of alcoholic and phenolic compounds dissolved in solvents devoid of the hydroxyl group. The results point conclusively to the fact that alcohols and phenols generally associate in benzene and naphthalene solutions, and that the association may be inhibited, partially or entirely, by the introduction of substituents in the ortho-position to the hydroxyl group in the case of phenolic compounds.

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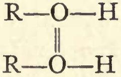
[1] Bülow and Sicherer, *Ber.*, 1901, **34**, 3920.

[2] Baeyer and Villiger, *Ber.*, 1901, **34**, 2685.

[3] See Raoult, *Ann. Chim. Phys.*, 1885, (vi.) (6) **4**, 401; Thomsen, *Ber.*, 1885, **18**, 1088; Vernon, *Chem. News*, 1891, **64**, 54; Ramsay and Shields, *Zeit. phys. Chem.*, 1893, **12**, 434; Brühl, *Ber.*, 1895, **28**, 2866.

[4] Beckmann, *Zeit. phys. Chem.*, 1890, **6**, 437.

Hewitt and Winmill[3] have recently studied the association of phenols in the liquid condition, and obtained some very interesting results. In the case of isomerides, the effect is most marked when an ortho-substituted compound is examined, and least marked in the case of the meta. The group NO_2 was found to inhibit association to the greatest extent. Hewitt and Winmill explain these cases of association by the assumption that the hydroxyl group possesses "residual affinity," and suggest the formula



$$\begin{array}{c}\mathrm{R{-}O{-}H}\\ \|\\ \mathrm{R{-}O{-}H}\end{array}$$

for the representation of the double molecules.

By substitution in the ortho position of a group also containing residual affinities of a fairly pronounced character, it is easy to see how association may be diminished.

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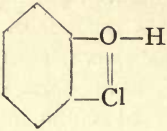
[1] See Ramsay and Shields, *Phil. Trans.*, 1893, **184**, 655; *Trans. Chem. Soc.*, 1893, **63**, 1089; Aston and Ramsay, *ibid.*, 1894, **65**, 167; *Zeit. phys. Chem.*, 1893, **12**, 433; 1894, **15**, 89; Ramsay, *ibid.*, 1894, **15**, 106.

[2] Auwers and his co-workers, *Zeit. phys. Chem.*, 1893, **12**, 689; 1894, **15**, 33; 1895, **18**, 595; 1896, **21**, 337; 1899, **30**, 300; 1900, **32**, 39; 1903, **42**, 513: *Ber.*, 1895, **28**, 2878; 1898, **31**, 3037.

[3] Hewitt and Winmill, *Trans. Chem. Soc.*, 1907, **91**, 441.

For example, *o*-chlorophenol will be represented by the formula



according to which association is almost impossible.

The fact that water crystallizes along with inorganic salts is also to be ascribed to the tetravalency of oxygen. We might therefore expect other substances, possessing divalent oxygen and a similar structure to water, to crystallize out in the same way. This is well known to be the case. For example, methyl alcohol crystallizes with calcium chloride, whereby the complex

$$CaCl_2 . 4CH_3OH$$

is formed.

Goldschmidt[1] believes that oxygen is tetravalent in organic acids and esters. Thus

$$R—C\equiv O—O—H$$

The ions are accordingly $R—C\equiv O^{\cdot}$ and $'OH$. Acetyl chloride is regarded as the chloride of the basic ion $CH_3 . CO^{\cdot}$, and acetic anhydride is a compound of the ions CH_3COO' and $CH_3CO^{\cdot}$, that is, its true name is acetyl acetate.

Julius Meyer[2] considers that the facts of autoxidation are best explained on the assumption that an unsaturated molecule is added to a molecule of oxygen, one atom of which is tetravalent. Hydrogen peroxide is regarded as $H_2O : O$, ozone as $O : O : O$, and so on. Such an assumption has much in its favour. It is in accord with the researches of Engler and Wild.[3] These investigators conclude, as the result of many experiments, that when the alkali metals are oxidized in the air, there is a direct combination of the metals with the oxygen molecule, a peroxide being formed, which slowly reacts with water, forming hydrogen peroxide and the metallic hydroxide. By assuming one of the atoms of oxygen to be tetravalent, we do not need to imagine that combination of the metal with the oxygen molecule is due to the breaking of one of the bonds holding the oxygen atoms together, thus:

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[1] Goldschmidt, *Zeit. Elektrochemie*, 1904, **10**, 221.

[2] Meyer, *J. pr. Chem.*, 1905, (2) **72**, 278.

[3] Engler and Wild, *Ber.*, 1897, **30**, 1669; but see Rengade, *Compt. rend.*, 1906, **143**, 1152; **144**, 753; de Forcrand, *ibid.*, **144**, 1321 and 1402.

$$\mathrm{O{=}O + 2Na \longrightarrow Na{-}O{-}O{-}Na}$$

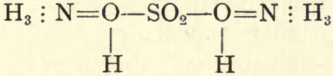
Rather is the action to be represented by the equation

$$\mathrm{O{=}O + 2Na \longrightarrow O{=}O{=}Na_2}$$

This explains the ease with which the second atom of oxygen is split off.

The assumption that the whole molecule of oxygen takes part in many other cases of oxidation has received strong support from the work of Manchot,[1] Bach,[2] Erdmann and Köthner,[3] and Engler,[4] and a similar explanation applies.

Cain [5] writes the formula for ammonium sulphate as



$$\mathrm{H_3 : N{=}\underset{\displaystyle H}{\underset{|}{O}}{-}SO_2{-}\underset{\displaystyle H}{\underset{|}{O}}{=}N : H_3}$$

in which two of the oxygen atoms are represented as tetravalent. The same author also regards ammonium hydroxide as

$$\mathrm{H_3N{=}OH_2}$$

Since ammonia gas dissolves in water with evolution of a considerable amount of heat, it is frequently assumed that ammonium hydroxide is the chief product, despite the comparatively poor conductivity. Hantzsch and Davidson [6] were the first to suggest a definite theory of hydrates of ammonia in solution, and Cain's [7] formula is in harmony with the same.

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[1] Manchot, *Ber.*, 1906, **39**, 1170; *Annalen*, 1902, **325**, 95.

[2] Bach, *Compt. rend.*, 1897, **124**, 2 and 951.

[3] Erdmann and Köthner, *Annalen*, 1897, **294**, 55.

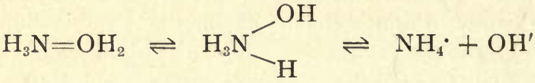
[4] Engler, *Ber.*, 1900, **33**, 1111.

[5] Cain, *Mem. Manchester Phil. Soc.*, 1904, **48**, xiv.

[6] Hantzsch and Davidson, *Ber.*, 1898, **31**, 1616.

[7] Cain, *op. cit.*

It seems reasonable to suppose, however, that the hydrated molecules undergo rearrangement to the hydroxylic form, until we have equilibrium between the two tautomers and ammonium ions and hydroxyl ions, thus :



$$H_3N{=}OH_2 \rightleftharpoons H_3N\genfrac{}{}{0pt}{}{\diagup OH}{\diagdown H} \rightleftharpoons NH_4^{\cdot} + OH'$$

By admitting the tetravalent nature of oxygen, we see that a close connection exists between the molecules of water and of ammonia, for both are unsaturated.[1] This affords an explanation for the fact that ammonia and water are frequently interchangeable in chemical compounds, for example $CuSO_4 . 5H_2O$ and $CuSO_4 . 5NH_3$. Further, Brill[2] has shown that liquid ammonia is slightly associated, although not to the same extent as water.

It has already been pointed out that organic compounds of divalent oxygen, for example, alcohols, can, like water, crystallize with inorganic salts. The same property is exhibited by organic derivatives of trivalent nitrogen. For example, a large number of salts has been prepared by Lang,[3] Pincussohn,[4] and others, containing pyridine of crystallization. A most remarkable example is afforded by cuprous chloride. In the presence of water this salt can absorb carbon monoxide, but not when perfectly dry. Lang found, however, that its solution in pyridine absorbs this gas with ease. Manchot and Friend[5] have since shown that not only may pyridine be replaced by other derivatives of trivalent nitrogen, such as aniline, *o*-toluidine, and piperidine, but that the amount of carbon monoxide absorbed per molecule of cuprous chloride is identical in each case with that absorbed in the presence of water.

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[1] Compare Friend, *Trans. Chem. Soc.*, 1908, **93**, 268.

[2] Brill, *Ann. Physik*, 1906, (iv.) **21**, 170; see Franklin and Kraus, *Amer. Chem. J.*, 1899, **21**, 8.

[3] Lang, *Ber.*, 1888, **21**, 1578.

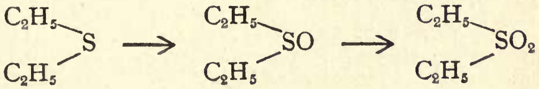
[4] Pincussohn, *Zeit. anorg. Chem.*, 1897, **14**, 379.

[5] Manchot and Friend, *Annalen*, 1908, **359**, 100.

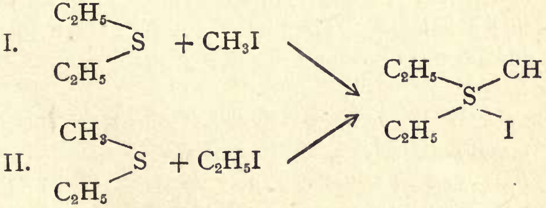
In aqueous solution the compound $CuCl . CO . 2H_2O$ is formed, in which the water is presumably attached by means of the unused valencies of the oxygen atoms. Although, owing to their instability, it was impossible to analyze the bodies formed in pyridine and other organic solutions, arguing by analogy it is highly probable that the two molecules of water were replaced by an equal number of molecules of the trivalent nitrogen derivative.

Not less interesting is the study of the valency of sulphur. Towards hydrogen this element is divalent. But whilst oxygen forms no compound with fluorine, sulphur readily yields a hexafluoride,[1] SF_6, which is remarkably stable and inert.

The variable nature of the valency of sulphur is well illustrated by its organic derivatives. Ethyl sulphide is oxidized by potassium permanganate or nitric acid to ethyl sulphoxide. If the oxidation be continued, ethyl sulphone [2] results. Thus :



In order to prove the equivalence of three of the first four valencies of sulphur, the work of Klinger and Maassen [3] is frequently cited. These investigators prepared methyldi-ethyl sulphonium iodide in two ways. Thus :



The same compound was obtained in both cases. Unless we argue that in one case rearrangement has taken place, during the reaction, to the more favoured position, it is clear that the three valencies, by which the alkyl groups are attached to the sulphur, must be equivalent. It is true that Krüger,[1] and Blaikie and Crum Brown[2] had done this before and had not obtained the same results, but this was, as Klinger and Maassen show, due to traces of impurity in the final products.

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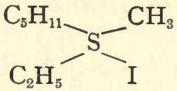
[1] Moissan and Lebeau, *Compt. rend.*, 1900, **130**, 865.

[2] Oefele, *Annalen*, **132**, 82.

[3] Klinger and Maassen, *Annalen*, 1888, **243**, 193.

A somewhat similar series of experiments was carried out by Brjuchonenko,[3] who prepared



in two different ways and obtained the same product.

The preparation of optically active derivatives of sulphur has proved exceedingly difficult. For a full account of this part of the subject, however, the reader is referred to Stewart's *Stereochemistry* (this series).

When chlorine is passed into an ice-cold solution of trimethylsulphonium iodide in glacial acetic acid, a tetrachloro-derivative is obtained.[4]

$$(CH_2)_3SI + 2Cl_2 = (CH_3)_3SClICl_3$$

This is not to be ascribed to the valency of sulphur suddenly changing to eight, but rather to the possession by the halogens of a higher valency than unity.

Dobbin and Masson,[5] a quarter of a century ago, studied a series of derivatives of sulphur, of the type $(CH_3)_3SX_3$, where X represents a halogen. They point out that three theories may be advanced to account for the constitution of these complexes.

1. They may be regarded as so-called molecular compounds, $(CH_3)_3SX . X_2$, in which X_2 is attached to the $(CH_3)_3SX$ in some such way as water of crystallization clings to many metallic salts. The halogens thus retain their monovalent nature, and the sulphur is but tetravalent. Such a formula, however, is not

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[1] Krüger, *J. pr. Chem.*, 1876, (2) **14**, 193.

[2] Blaikie and Crum Brown, *Chem. News*, 1878, **37**, 130.

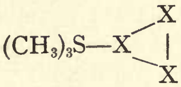
[3] Brjuchonenko, *Ber.*, 1898, **31**, 3176.

[4] E. A. Werner, *Trans. Chem. Soc.*, 1906, **89**, 1629.

[5] Dobbin and Masson, *Trans. Chem. Soc.*, 1885, **47**, 56.

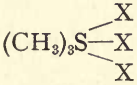
in accordance with the decomposition of these bodies by heat.

2. While postulating the tetravalent nature of the sulphur atom, the halogens may be regarded as divalent or trivalent, thus:



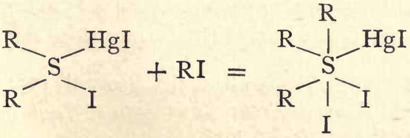
This would not only account for the decomposition of the complex by heat, but it would also explain the power which these bodies exhibit, of uniting with ammonia. Thus, for example, $(CH_3)_3SIBr_2 . 2NH_3$. On the other hand, this arrangement scarcely explains the fact that trimethylsulphine sulphate can combine with bromine and chlorine.

3. Dobbin and Masson conclude that the true formula for these complexes is



in which the sulphur functions as a hexavalent atom, whereas the halogens remain monovalent. This is regarded by the authors as being free from the objections mentioned above.

Hilditch and Smiles[1] have recently studied the accelerating influence of mercuric iodide on the formation of sulphonium iodides. Smiles[2] had already shown that mercuric iodide could form additive products of the type $R_2S . HgI_2$. It seems most probable, therefore, that it is these complexes which react with the alkyl iodide, the valency of the sulphur changing from four to six. The equation given by the authors is



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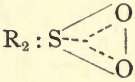
[1] Hilditch and Smiles, *Trans. Chem. Soc.*, 1907, **91**, 1394.

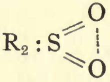
[2] Smiles, *Trans. Chem. Soc.*, 1900, 77, 163.

Reference may here be made, also, to the work of Pope and Neville[1] on the hexavalent nature of sulphur and selenium.

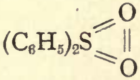
Pickard and Kenyon[2] have drawn attention to the fact that diphenyl sulphoxide, $(C_6H_5)_2SO$, combines with metallic salts, whereas no such compounds with diphenyl sulphone, $(C_6H_5)_2SO_2$, could be obtained. Similarly Hermann[3] obtained an additive compound of dibenzyl sulphoxide with hydrochloric acid. Pickard and Kenyon suggest "that in the sulphone the oxygen and sulphur atoms are united in a ring in such a manner that any residual valencies of the same are mutually satisfied." Thus:



where the dots represent subsidiary valencies. They regard the formula



as less likely. Another explanation for this phenomenon is to be found in the tetravalency of oxygen. In diphenyl sulphoxide, the oxygen is divalent and unsaturated. Consequently addition of other groups becomes possible. In diphenyl sulphone, however, the oxygen atoms may be regarded as tetravalent, thus:



Combination with other groups is thereby rendered difficult. The case is exactly analogous to that of sulphur di- and trioxides, the latter of which shows a strong tendency to associate to double molecules, whereas the former does not.[4]

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[1] Pope and Neville, *Trans. Chem. Soc.*, 1902, **81**, 1552.

[2] Pickard and Kenyon, *Trans. Chem. Soc.*, 1907, **91**, 896.

[3] Hermann, *Ber.*, 1906, **39**, 3815.

[4] This latter phenomenon is discussed fully by Friend, *Trans. Chem. Soc.*, 1908, **93**, 266.

As we have already seen in an earlier chapter,[1] selenium and tellurium show a marked resemblance both to one another and to sulphur. Each is divalent with respect to hydrogen, and hexavalent with regard to fluorine.

In their organic derivatives, selenium and tellurium usually function either as divalent or tetravalent elements. This will be clear from the following table.[2]

Organic Derivatives of Selenium and Tellurium

$Se(C_2H_5)_2$

$Se(C_2H_5)_3OH$ [3]

$$\left.\begin{array}{l} Se(CH_3)_2Cl_2 \\ Se(C_6H_5 . CH_2)_2Cl_2 \end{array}\right\}$$ [4]

$$\left.\begin{array}{l} Se(C_2H_5)_2Cl_2 \\ Se(C_2H_5)_3Cl \end{array}\right\}$$ [5]

$$\left.\begin{array}{l} Se(CH_2COCH_3)_2Cl_2 \\ Se(CH_2COC_6H_5)_2Cl_2 \end{array}\right\}$$ [6]

$Te(C_2H_5)_2$ [7]

$Te(C_2H_5)_3I$

$Te(C_6H_4OCH_3)_2$

$Te(C_6H_5)_2Br_2$ [8]

We now pass on to the study of chromium.

Two chlorides of chromium are known, namely the chromous and chromic. According to the researches of Nilson and Pettersson,[9] these are represented by the formulæ

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[1] See Chapter V.

[2] This table is only illustrative; it is not claimed to be in any sense exhaustive.

[3] Pieverling, *Ber.*, 1876, **9**, 1469.

[4] Jackson, *Annalen*, 1875, **179**, 1.

[5] Ratke, *Annalen*, 1869, **152**, 181.

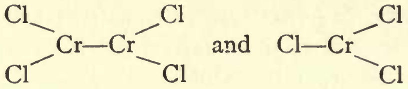
[6] Michaelis and Kunckell, *Ber.*, 1897, **30**, 2823.

[7] Marquardt and Michaelis, *Ber.*, 1888, **21**, 2042; Becker, *Annalen*, **180**, 263; Cahours, *Ann. Chim. Phys.*, 1877, (5) **10**, 50.

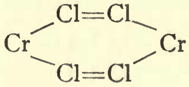
[8] Krafft and Lyons, *Ber.*, 1894, **27**, 1770.

[9] Nilson and Pettersson, *Zeit. phys. Chem.*, 1888, **2**, 674.

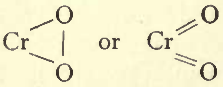
Cr_2Cl_4 and $CrCl_3$ respectively. In each of these bodies chromium may be regarded as trivalent, as is evident if the following graphical formulæ be attributed to them, namely



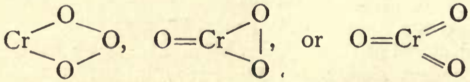
In view of the fact that so many metallic chlorides exhibit a tendency to associate, and that the chromous and chromic salts exhibit such different properties, it seems more reasonable to consider the chromium in chromous chloride as divalent. Thus:



A study of the oxygen compounds of chromium has led chemists to the conclusion that the latter element can function both as a tetravalent and a hexavalent atom. Manchot and Kraus[1] in 1906 prepared a dioxide by heating $Cr_2(HO)_6$ in dry oxygen at 320–345° for several days, and gave it the formula CrO_2. Here the chromium may be either divalent or tetravalent. Thus:



Manchot evidently prefers the latter scheme, and regards the dioxide as a proof of the tetravalency of chromium. In chromic anhydride, CrO_3, analogous to sulphur tri-oxide, chromium is generally regarded as hexavalent. But it might also be di- or tetra-valent. Thus:



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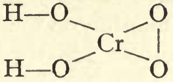
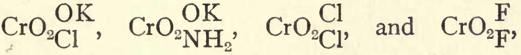
[1] Manchot and Kraus, *Ber.*, 1906, **39**, 3512.

Manchot is of the opinion that the middle formula is correct, and for chromic acid he writes[1]



As we have already seen, the hexafluoride of sulphur, SF_6, confirms the hexavalent nature of that element. But no corresponding fluoride of chromium has as yet been prepared, although the trifluoride, CrF_3, is well known. In potassium chlorochromate, potassium amidochromate, and chromyl chloride and fluoride, whose formulæ are usually given as



$$CrO_2\substack{OK\\Cl},\quad CrO_2\substack{OK\\NH_2},\quad CrO_2\substack{Cl\\Cl},\quad \text{and}\quad CrO_2\substack{F\\F},$$

respectively, the chromium may be regarded as either tetravalent or hexavalent.

Potassium chromate, K_2CrO_4, crystallizes according to the rhombic system, and is isomorphous with potassium sulphate. It seems reasonable to argue that if in the latter case sulphur is hexavalent, then the chromium in the former is also hexavalent.

A number of complex chromium derivatives have been discovered during the past few years, and not a few cases of stereo-isomerism have been met with. It is beyond the scope of this work to deal with these here.[2]

The next element to engage our attention is molybdenum, which apparently exhibits a very variable valency. The highest chloride known contains five atoms of chlorine to every one of molybdenum. Vapour density considerations lead us to attribute to it the simple formula $MoCl_5$. It easily parts with chlorine, whereby the tetrachloride, $MoCl_4$, results. Two other chlorides are known, namely the dichloride, $MoCl_2$, and trichloride, $MoCl_3$. Although these molecules exhibit association in the vapour state, this is probably due to the trivalent nature of the chlorine.

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[1] Manchot, *Über Sauerstoff Activierung:* "Verhandlungen der Phys. Med. Ges.," Würzburg, 1908, **39**, 236.

[2] The reader, desirous of perusing a short account of the same, is referred to Dr. Stewart's work, entitled *Stereochemistry.*

Ruff and Eisner[1] have recently prepared a hexafluoride, MoF_6, by the action of fluorine on the finely divided metal at 60–70° C. The oxyfluorides $MoOF_4$ and MoO_2F_2 have also been prepared.

Tungsten differs from molybdenum in possessing a hexachloride, to which the formula WCl_6 has been assigned. This body readily parts with chlorine, yielding the pentachloride the formula of which, WCl_5, is confirmed by vapour density determinations.[2]

Ruff and Eisner[3] have obtained the gaseous hexafluoride WF_6, by the interaction of tungsten hexachloride and hydrofluoric acid. The oxyfluorides WOF_4 and WO_2F_2, and the oxychloride $WOCl_4$, are also known.

---

[1] Ruff and Eisner, *Ber.*, 1907, **40**, 2926.

[2] Debray, *Compt. rend.*, 1865, **60**, 820; Rieth, *Ber.*, 1870, **3**, 666.

[3] Ruff and Eisner, *Ber.*, 1905, **38**, 742; *Zeit. anorg. Chem.*, 1907, **52**, 256.

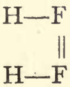
XVI

THE VALENCY OF THE ELEMENTS OF GROUP VII

THE study of the valency of the elements of this group is of especial interest.

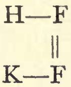
As we might expect, fluorine differs from the other halogens in many of its properties. Thus, for example, whilst it forms a very stable compound with hydrogen, no compound of fluorine and oxygen is known.

Hydrogen fluoride is generally represented by the formula HF. Nevertheless it is certain that its molecule is at least double.[1] An acid potassium salt, KHF_2, is also known, and unless we attribute a higher valency than unity to hydrogen and potassium, we must infer that fluorine is not monovalent. The graphical formulæ to be given to these bodies are probably



$$\begin{array}{l}H-F\\ \quad\ \ \|\\ H-F\end{array}$$

and



$$\begin{array}{l}H-F\\ \quad\ \ \|\\ K-F\end{array}$$

respectively, where the fluorine is represented as trivalent. In hydrofluosilicic acid, and several other molecules of like constitution, we have already assumed the presence of trivalent fluorine.[2]

Chlorine is uniformly monovalent in its hydride, for hydrogen chloride shows no tendency to associate to double molecules. We have already seen, however, that the association of metallic chlorides, as, for example, those of sodium, monovalent copper and mercury, aluminium, etc., is probably to be attributed to the trivalent nature of chlorine.

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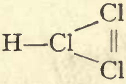
[1] See Vernon, *Chem. News*, 1891, **64**, 54; Mallet, *ibid.*, 1881, **44**, 164; Jäger, *Zeit. anorg. Chem.*, 1901, **27**, 28; Pellini and Pegoraro, *Zeit. Elektrochem.*, 1907, **13**, 621; Kremann and Decolle, *Monatsh.*, 1907, **28**, 917; Paternó and Peratoner, *Chem. Zent.*, 1891, 306; compare Thorpe and Hambly, *Trans. Chem. Soc.*, 1889, **55**, 163.

[2] See Chapter IX.

Mellor[1] has obtained evidence of the existence of HCl_3, which may be regarded as



recalling the constitution of hydrazoic acid.

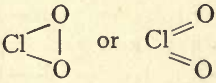
Chlorine monoxide, Cl_2O, dissolves in water, yielding hypochlorous acid, HClO. If we write the molecule of this latter substance as

$$H—O—Cl$$

it is difficult to see why it should so readily lose oxygen on being warmed. This difficulty may be overcome by assuming that the chlorine is trivalent, thus :

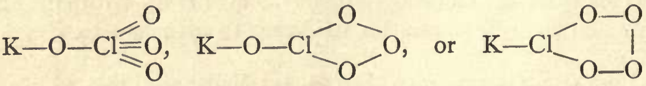
$$H—Cl=O$$

In chlorine peroxide we may have either divalent or tetravalent chlorine, thus :



The former scheme illustrates the peroxide properties of the molecule better than the latter.

Several schemes can be suggested for potassium perchlorate. Thus :



The first of these has the disadvantage of attributing to chlorine a very high valency, namely seven. On the other hand, it affords an explanation for the interesting observation[1] that the perchlorates of potassium, rubidium, caesium and ammonium, and the permanganates of the same, form an ismorphous group, for potassium permanganate is usually assumed to have the constitution represented by the formula

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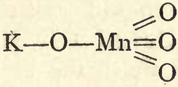
[1] Mellor, *Trans. Chem. Soc.*, 1901, **79**, 216; see Jakowkin, *Zeit. phys. Chem.*, 1899, **29**, 635; Berthelot, *Compt. rend.*, 1880, **91**, 191; *Ann. Chim. Phys.*, 1875, (5) **5**, 339; (5) **22**, 49.



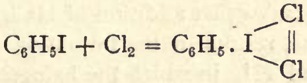
$$K{-}O{-}Mn\begin{matrix} \nearrow\!\!\!\!= O \\ \equiv O \\ \searrow\!\!\!\!= O \end{matrix}$$

The middle formula has little in its favour, but the third, which does not assume the presence of a hydroxyl group in the acid, explains the ease with which potassium chloride is formed on heating.

With regard to hydrogen, bromine is monovalent. It yields with fluorine a trifluoride, BrF_3.[2] Here, and in potassium tribromide, KBr_3,[3] we are evidently dealing with trivalent bromine.

In hydriodic acid, iodine is monovalent. Nevertheless iodine pentafluoride, IF_5, has been isolated by Gore.[4]

Numerous organic derivatives have been obtained in which iodine functions as a mono-, tri-, and penta-valent atom. When chlorine is introduced into a solution of iodobenzene, C_6H_5I, in chloroform, the iodine is not replaced, but an addition product, phenyl iododichloride, $C_6H_5ICl_2$, is produced,[5]



$$C_6H_5I + Cl_2 = C_6H_5 . I \begin{matrix} \diagup Cl \\ \quad \| \\ \diagdown Cl \end{matrix}$$

This, when shaken with caustic alkali, yields iodosobenzene

$$C_6H_5ICl_2 + 2KOH = C_6H_5IO + 2KCl + H_2O$$

---

[1] Barker, *Trans. Chem. Soc.*, 1906, **89**, 1157.

[2] Prideaux, *Proc. Chem. Soc.*, 1905, **21**, 240.

[3] Worley, *Trans. Chem. Soc.*, 1905, **87**, 1107.

[4] Gore, *Chem. News*, 1871, **24**, 291; analyzed by Moissan, *Compt. rend.*, 1902, **135**, 563.

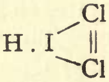
[5] Willgerodt, *J. pr. Chem.*, 1886, ii. **33**, 154.

When heated alone or boiled with water, iodosobenzene yields iodoxybenzene

$$2C_6H_5IO = C_6H_5I + C_6H_5IO_2$$

a substance which behaves like a peroxide. On heating to about 227° it explodes. When a mixture of iodoso- and iodoxy-benzene is shaken with moist silver oxide, diphenyl-iodonium hydroxide, $(C_6H_5)_2I \, . \, OH$, is produced. This base forms definite salts, in which the iodine retains its trivalent nature. Not the least interesting of these is the iodide, $(C_6H_5)_2 I \, . \, I$, which is polymeric with iodobenzene, and is converted into the same on warming. For much of our knowledge of the constitution of the organic derivatives of iodine we are indebted to the researches of Victor Meyer and his pupils.[1]

Thiele and Peter[2] prepared methyl iododichloride, CH_3ICl_2, by the action of chlorine on a solution of methyl iodide in carbon tetrachloride and light petroleum, cooled to about − 75° C. This body is similar to Schützenberger's[3] compound, $ICl \, . \, HCl$, to which the graphical formula



may be given.

Tinkler[4] concludes that addition of HCl, HBr, or HI, to a solution of iodine, results in the formation of the complexes $HClI_2$, $HBrI_2$, and HI_3, in which the halogens are presumably trivalent.

Thiele and Peter[5] have obtained a most interesting compound by the action of chlorine on chloro-iodofumaric acid, and ascribe to it the formula

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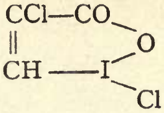
[1] V. Meyer and co-workers, *Ber.*, 1893, **26**, 1354 and 1727; 1894, **27**, 1592.

[2] Thiele and Peter, *Ber.*, 1905, **38**, 2842.

[3] Schützenberger, *Compt. rend.*, 1877, **84**, 389; see E. A. Werner, *Trans. Chem. Soc.*, 1906, **89**, 1631.

[4] Tinkler, *Trans. Chem. Soc.*, 1907, **91**, 1002.

[5] Thiele and Peter, *Ber.*, 1905, **38**, 2842.



Here the three valencies of iodine are distributed between carbon, chlorine, and oxygen, an arrangement which is almost unique.

The only metal of this group to receive consideration is manganese. It forms both acidic and basic oxides. In the latter the metal is usually di- or tri-valent. In the former it may be heptavalent, as in potassium permanganate, to which reference has already been made.

XVII

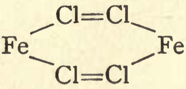
THE VALENCY OF THE ELEMENTS OF GROUP VIII

THE study of the chlorides of iron has yielded similar results to those obtained in the case of chromium. Deville and Troost[1] believed, from vapour density considerations, that the formula for the ferric salt was Fe_2Cl_6. V. Meyer[2] showed, however, that between 750° and 1077° C. the molecules are single. As with aluminium chloride, the vapour density varies with the temperature, the degree of association increasing as the temperature falls.

Ferrous chloride yielded values intermediate between those required for the formulæ $FeCl_2$ and Fe_2Cl_4, when volatilized in an atmosphere of hydrogen chloride. Here, therefore, we have another condition of equilibrium represented by the equation

$$2\ FeCl_2 \rightleftharpoons Fe_2Cl_4$$

Werner[3] has shown that in solution the molecules of ferrous chloride are single, and that the iron is therefore truly divalent. The associated gaseous molecules may therefore be represented by the scheme



In iron tetra- and penta-carbonyls,[4] $Fe(CO)_4$, and $Fe(CO)_5$, iron might be assumed to have eight and ten valencies respectively. It is probable, however, that the metal is still only divalent, the CO-groups being arranged in a ring (see nickel).

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[1] Deville and Troost, *Ann. Chim. Phys.*, 1860, (3) **58**, 280.

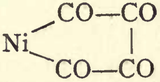
[2] V. Meyer, *Ber.*, 1884, **17**, 1335.

[3] Werner, *Zeit. anorg. Chem.*, 1897, **15**, 1.

[4] Dewar and Jones, *Proc. Roy. Soc.*, 1905, **76** A, 558 ; 1907, **79** A, 66 ;

As we have already seen in an earlier chapter,[1] the properties of cobalt are intermediate between those of iron and nickel. It resembles iron in that it forms two classes of salts, namely cobaltous and cobaltic, in which the metal is di- and tri-valent respectively. Cobalt shows a remarkable power of forming complexes with ammonia, to which the name cobaltammines has been given. These will be considered later.[2]

Nickel apparently functions as a divalent atom only. In the tetracarbonyl,[3] $Ni(CO)_4$, the metal might be regarded as octavalent. There is no reason, however, why the carbon atoms should not be arranged in a ring. Thus:



by which scheme nickel retains its divalency, and a structure recalling that of leuconic acid is obtained. This is apparently supported by the fact that the action of chlorine on nickel carbonyl takes place according to the equation[4]

$$Ni(CO)_4 + Cl_2 = NiCl_2 + 4CO$$

Osmium apparently functions as an octavalent atom in the tetroxide OsO_4, as does ruthenium in RuO_4. The potassium salts of osmic and ruthenic acids, namely K_2OsO_4 and K_2RuO_4, remind us of potassium sulphate, K_2SO_4, and judging by analogy we are led to impute a valency of six to osmium and ruthenium.

Mond, *Chem. Zentr.*, 1892, ii, 1062; Mond and his co-workers, *Trans. Chem. Soc.*, 1891, **59**, 604 and 1090; *British Assoc.*, 1891.

[1] See Chapter V.

[2] See Chapter XVIII.

[3] Mond and Nasini, *Rend. Acad. Lincei.*, 1891, **7**, 411; *Zeit. phys. Chem.*, **8**, 150; Mond, Langer, and Quincke, *Chem. News*, 1890, **62**, 97; Mond, *Chem. Zentr.*, 1892, ii, 1062; Berthelot, *Compt. rend.*, 1891, **112**, 1343.

[4] Dewar and Jones, *Trans. Chem. Soc.*, 1904, **85**, 203.

In potassium per-ruthenate, $KRuO_4$, analogous to potassium permanganate, ruthenium possibly functions as a heptavalent atom.

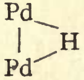
L. Wöhler and Witzmann[1] have recently investigated the oxides of iridium, and conclude that the monoxide, IrO, does not exist. The sesquioxide, Ir_2O_3, dioxide, IrO_2, and trioxide, IrO_3, are described, in which the metal is apparently tri-, tetra-, and hexa-valent, respectively. Arguing by analogy with K_2GeF_6,[2] etc., we may attribute to iridium a valency of four in the salt Na_2IrCl_6, as we do in the simple tetrachloride, $IrCl_4$.

In Ir_2Cl_6 the metallic atom is presumably trivalent, as in the analogous salts of iron and aluminium.

Two chlorides of platinum are known, namely, the dichloride, $PtCl_2$, and the tetrachloride, $PtCl_4$, from which we infer that, like tin, platinum can function as a divalent and a tetravalent atom. This would seem to be confirmed by the existence of two oxides, PtO and PtO_2. The platinum chlorides exhibit a strong tendency to unite with other salts to form very complex molecules, but these cannot be dealt with here.

Palladium apparently forms but two oxides, namely PdO and PdO_2,[3] in which the metal is apparently di- and tetra-valent respectively. Palladium tetrachloride resembles the corresponding platinum and iridium salts in its power of uniting with alkali chlorides to form complex derivatives, for example, K_2PdCl_6 and $(NH_4)_2PdCl_6$.

It is well known that palladium readily absorbs or occludes large volumes of hydrogen gas. Troost and Hautefeuille[4] believed that a compound of the formula Pd_2H was formed. This raised the interesting question as to the possibility of hydrogen functioning as a divalent atom. Thus:



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[1] L. Wöhler and Witzmann, *Zeit. anorg. Chem.*, 1908, **57**, 323.

[2] See Chapter XII.

[3] Wöhler and König, *Zeit. anorg. Chem.*, 1905, **46**, 323.

[4] Troost and Hautefeuille, *Ann. Chim. Phys.*, 1874, (5) **2**, 279; *Compt. rend.*, 1874, **78**, 686.

Further researches have shown, however, that no compound of palladium and hydrogen in the ordinary acceptation of the word is formed.[1]

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[1] See Hoitsema, *Zeit. phys. Chem.*, 1895, **17**, 1; Dewar, *Phil. Mag.*, 1874, (4) **17**, 324 and 343; Mond, Ramsay and Shields, *Proc. Roy. Soc.*, 1897, **62**, 290. A clear statement of the whole case is given by Dr. Findlay in his work entitled *The Phase Rule* (this series), 1904, p. 176.

XVIII

WERNER'S THEORY[1]

AFTER a very careful and thorough study of the complex ammino-compounds, Werner was led to suggest a new theory of valency, by which he was able to group these substances into well-defined classes. The success which rewarded his efforts in this field led him to apply his theory to the study of simple compounds.

Werner distinguishes two kinds of valency, known as Principal and Auxiliary. The principal valencies correspond to those generally accepted as belonging to the elements. The auxiliary valencies are somewhat vague and ill-defined. They differ from the principal valencies in their smaller energy content, and it is regarded as possible for several of them to unite and form a principal valence. Groups bound by auxiliary valencies are incapable of dissociation. A few examples will make this clear.

Werner writes

$$H_3N \ldots . H . Cl$$

for ammonium chloride, where the dotted line represents the auxiliary valencies joining the hydrogen to the nitrogen. The hydrogen atom is thus incapable of dissociation, whereas the chlorine atom is free. This formula further explains the readiness with which ammonia and hydrochloric acid unite.

Several objections may, however, be raised. The nitrogen is here represented as tetravalent and the hydrogen as divalent, assumptions for which we have no warrant. Further, the fourth hydrogen atom is not attached to the nitrogen in the same way as the other three. This would lead us to expect some difference in its chemical properties. But the researches of Victor Meyer[1] on the alkylammonium iodides indicate that no such difference in reality exists.

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[1] A very complete account of this theory is given in Werner's interesting little work entitled *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie*, 1905, Braunschweig.

Finally, as Arrhenius[2] has pointed out, if we replace hydrochloric acid by a weak acid, for example, acetic, the degree of ionisation of this weak acid is *increased* by neutralization with ammonia. This, of course, should not occur if we are simply dealing with the addition of an NH_3-group to the hydrogen atom of the acid.

Tetramethylammonium hydroxide, $(CH_3)_4NOH$, prepared by the action of moist silver oxide on the iodide, $(CH_3)_4NI$, is a strong base, and its degree of ionisation is of the same order as that of its salts. Yet according to Werner's theory it is to be regarded as an addition product of trimethylamine and methyl alcohol, which latter is probably even less dissociated than water itself.

As has already been stated, however, it is in its application to the complex ammino-compounds that Werner's theory has been most successful and suggestive. By arranging these in well-defined groups and drawing up graphical formulæ to represent their constitution, it has been possible to predict the discovery of many new substances. Thus an enormous impetus to research in this direction has been afforded to chemists, who have not been slow to avail themselves of the opportunity. The result is that such a vast amount of new material has been accumulated, that a whole volume would be required for its treatment. In the following pages, therefore, we cannot do more than give an outline of the ingenious theory, to which Werner has given expression, in its application to these complex derivatives.

Two compounds are known having the composition

$$PtCl_4(NH_3)_2$$

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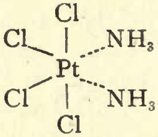
[1] See Chapter XIII.

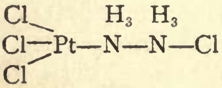
[2] Arrhenius, *Theorien der Chemie*, Leipzig, 1906.

Neither isomer shows any appreciable dissociation in aqueous solution. It is therefore assumed that the six radicles are attached directly to the platinum atom, the four chlorine atoms by principal, and the two NH_3-groups by auxiliary valencies. Thus :

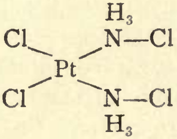


It will be clear that if these radicles are arranged spatially round the platinum atom, two different schemes are possible, namely, one in which the two NH_3-groups are adjacent, as at RR_1 or R_1R_2 (Fig. 3), and one in which they are opposite to each other, as at RR_5 or R_1R_3. These represent the two isomers known.

The formulæ, which must be employed according to Cleve and Jörgensen, who have adhered to the usually accepted views on valency, are



and



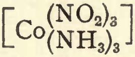
These formulæ are not only clumsy, but fail to explain the undissociable nature of the complexes. They have the advantage, however, of not attributing to platinum a greater valency than four, and the necessity of introducing tetravalent nitrogen is done away with.

Further, it is difficult to see why, if the chlorine atoms in Werner's formulæ are incapable of dissociation simply because they are attached to the platinum atom direct, in the case of potassium chloride, where the chlorine is attached with equal directness to the metal, we have to deal with a highly ionisable salt.

A second example is afforded by the complex

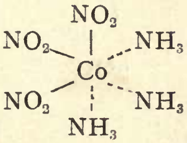
$$Co(NO_2)_3(NH_3)_3$$

which again is incapable of ionisation. Werner therefore writes the formula as



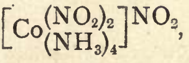
$$\left[\mathrm{Co}\begin{matrix}(NO_2)_3\\(NH_3)_3\end{matrix}\right]$$

where the six groups are supposed to be spatially arranged round the cobalt atom. The three NO_2-groups are attached directly to the cobalt by principal valencies, and the NH_3-groups by auxiliary valencies. Thus:

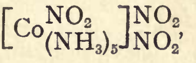


These six groups constitute what is known as the First or Undissociable Zone.

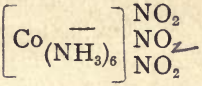
If, now, we act on this substance with ammonia, the following substitution products can be obtained:—



$$\left[\mathrm{Co}\begin{matrix}(NO_2)_2\\(NH_3)_4\end{matrix}\right]NO_2,$$



$$\left[\mathrm{Co}\begin{matrix}NO_2\\(NH_3)_5\end{matrix}\right]\begin{matrix}NO_2\\NO_2\end{matrix},$$



$$\left[\mathrm{Co}\begin{matrix}—\\(NH_3)_6\end{matrix}\right]\begin{matrix}NO_2\\NO_2\\NO_2\end{matrix}$$

in which one, two, and three NO_2-groups, respectively, can become ions, having been expelled from the first zone by a like number of NH_3-groups. They now form the Second or Dissociable Zone, and hover around the nucleus in a somewhat indefinite manner. The number of radicles in the first zone attached directly to the metal, whether by principal or auxiliary valencies, is known as the *co-ordinate number*, and in almost every well-established case is either four or six.

The ammino-complexes are usually classified as follows:—

A.:—Types in which the co-ordinate number is six. The radicles are supposed to be at the corners of a regular octahedron, in the centre of which the metallic atom remains.

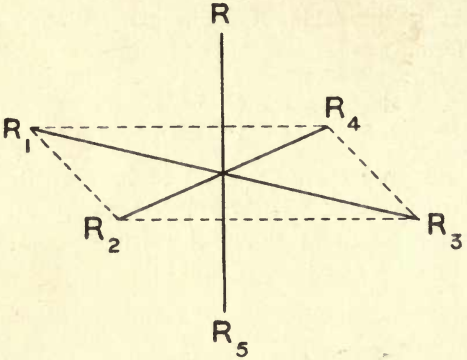


FIG. 3.

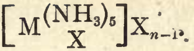
1. **Type** $[M(NH_3)_6]X_n$.

All members of this type contain a complex positive ion, consisting of a central metallic atom, surrounded by six NH_3-groups. They are therefore known as hexammines. The valency of the complex radicle is the same as that of the central metallic atom, for the NH_3-groups are regarded as attached by auxiliary valencies, thus leaving the principal valencies of the metal free.

All the negative radicles can become ions, and, in the case of the chlorides, may be precipitated by silver nitrate in the cold.

At present three classes belonging to this type are known, namely those in which M represents a tetravalent, trivalent, and divalent metal respectively. The following examples will make this clear :—

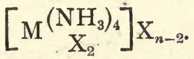
Class 1. $n = 4$. $[Pt(NH_3)_6]Cl_4$.
Class 2. $n = 3$. $[Co(NH_3)_6]Cl_3$.
Class 3. $n = 2$. $[Ni(NH_3)_6]Cl_2$.



2. **Type** $\left[\mathrm{M}{}^{(\mathrm{NH_3})_5}_{\mathrm{X}}\right]\mathrm{X}_{n-1}$.

The peculiarity of this type is that although the complex contains *n* negative radicles, only *n* − 1 of these are ionisable. One radicle is therefore assumed to have replaced an NH_3-group in the inner zone; and to have thus become directly attached to the central metallic atom. It is therefore incapable of ionisation. Since five NH_3-groups remain in the complex positive ion, the salts are known as the acidopentammines.

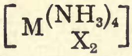
The large majority of complexes of this type are derivatives of trivalent metals, such as cobalt, chromium, rhodium, and iridium. Since the first compounds studied had a reddish-violet colour, the general name of purpureo-salts has been given to this group.



3. **Type** $\left[\mathrm{M}{}^{(\mathrm{NH_3})_4}_{\mathrm{X_2}}\right]\mathrm{X}_{n-2}$.

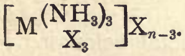
On the removal of a molecule of ammonia from the acidopentammines, one more negative radicle enters the inner zone, and a diacidotetrammino-salt results.

When *n* is equal to 2, the molecule



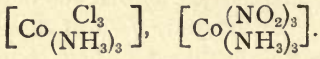
$$\left[\mathrm{M}{}^{(\mathrm{NH_3})_4}_{\mathrm{X_2}}\right]$$

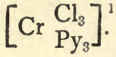
shows no appreciable ionisation, since there are no negative radicles in the outer zone. Consequently all the radicles are attached directly to the central metallic atom. Whilst such examples are rare, many complexes are known belonging to this type, where the central atom is trivalent. Among the most important of these are derivatives of cobalt and chromium. Several compounds of tetravalent platinum belonging to this type have also been prepared.



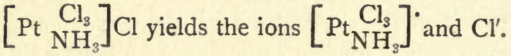
4. **Type** $\left[\mathrm{M}{}^{(\mathrm{NH_3})_3}_{\mathrm{X_3}}\right]\mathrm{X}_{n-3}$.

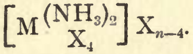
Members of this type are known as triacidotriammines. When *n* is equal to three, that is, when the central atom is trivalent, the complex ceases to show ionisation in aqueous solution. For example:

a. Cobalt: 
$\left[\mathrm{Co}\genfrac{}{}{0pt}{}{\mathrm{Cl_3}}{\mathrm{(NH_3)_3}}\right]$, $\left[\mathrm{Co}\genfrac{}{}{0pt}{}{\mathrm{(NO_2)_3}}{\mathrm{(NH_3)_3}}\right]$.

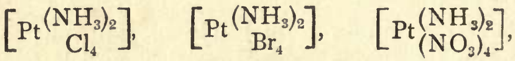
b. Chromium: 
$\left[\mathrm{Cr}\genfrac{}{}{0pt}{}{\mathrm{Cl_3}}{\mathrm{Py_3}}\right]$.[1]

When the central metallic atom is tetravalent, two ions are formed on solution in water, namely, a complex positive ion, and a simpler negative ion. Thus, for example,


$\left[\mathrm{Pt}\genfrac{}{}{0pt}{}{\mathrm{Cl_3}}{\mathrm{NH_3}}\right]\mathrm{Cl}$ yields the ions $\left[\mathrm{Pt}\genfrac{}{}{0pt}{}{\mathrm{Cl_3}}{\mathrm{NH_3}}\right]^{\cdot}$ and Cl′.


5. **Type** $\left[\mathrm{M}\genfrac{}{}{0pt}{}{\mathrm{(NH_3)_2}}{\mathrm{X_4}}\right]\mathrm{X}_{n-4}$.

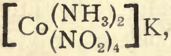
As examples of this type, the platinidiammines may be quoted

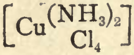

$\left[\mathrm{Pt}\genfrac{}{}{0pt}{}{\mathrm{(NH_3)_2}}{\mathrm{Cl_4}}\right]$, $\left[\mathrm{Pt}\genfrac{}{}{0pt}{}{\mathrm{(NH_3)_2}}{\mathrm{Br_4}}\right]$, $\left[\mathrm{Pt}\genfrac{}{}{0pt}{}{\mathrm{(NH_3)_2}}{\mathrm{(NO_3)_4}}\right]$,

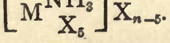
in which platinum functions as a tetravalent element.

These complexes dissolve in water without exhibiting electrolytic dissociation.

If the valency of the central metallic atom is less than four, the co-ordinated group becomes negative in character, and the radicle in the outer zone becomes a positive ion. For example:

a. Cobalt: 
$\left[\mathrm{Co}\genfrac{}{}{0pt}{}{\mathrm{(NH_3)_2}}{\mathrm{(NO_2)_4}}\right]\mathrm{K}$, (Erdmann's salt) with one positive ion.

b. Copper: 
$\left[\mathrm{Cu}\genfrac{}{}{0pt}{}{\mathrm{(NH_3)_2}}{\mathrm{Cl_4}}\right]\mathrm{(NH_4)_2}$, with two positive ions.


6. **Type** $\left[\mathrm{M}\genfrac{}{}{0pt}{}{\mathrm{NH_3}}{\mathrm{X_5}}\right]\mathrm{X}_{n-5}$.

No salts of a hexavalent metal belonging to this type are known.

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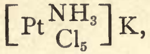
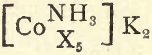
[1] Py stands for one molecule of pyridine.

When M is tetravalent, the complex group becomes negative in character, as, for example, in Cossa's salt



$$\left[\mathrm{Pt}\genfrac{}{}{0pt}{}{\mathrm{NH_3}}{\mathrm{Cl_5}}\right]\mathrm{K},$$

which contains one positive ion in the outer zone. The corresponding cobalt salt



$$\left[\mathrm{Co}\genfrac{}{}{0pt}{}{\mathrm{NH_3}}{\mathrm{X_5}}\right]\mathrm{K_2}$$

is not known.

7. **Type** $[MX_6]$.

This is, strictly speaking, no ammino-type at all, for the last NH_3-group has now been replaced by a negative radicle. As examples of this type we have:

a. Potassium platinichloride, $[Pt\,Cl_6]K_2$.
b. Potassium cobaltinitrite, $[Co(NO_2)_6]K_3$.
c. Potassium cadmium chloride, $[Cd\,Cl_6]K_4$.

B.:—Types in which the co-ordinate number is four. The radicles are supposed to lie in a plane round the central metallic atom, the vertical axis being absent.

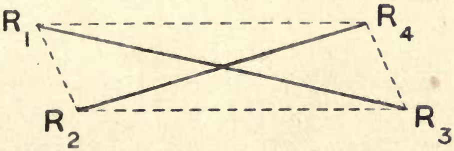
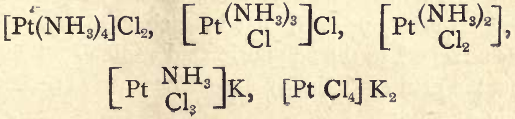


FIG. 4.

As examples of these, the following derivatives of divalent platinum may be cited:—



$$[\mathrm{Pt(NH_3)_4}]\mathrm{Cl_2},\quad \left[\mathrm{Pt}\genfrac{}{}{0pt}{}{\mathrm{(NH_3)_3}}{\mathrm{Cl}}\right]\mathrm{Cl},\quad \left[\mathrm{Pt}\genfrac{}{}{0pt}{}{\mathrm{(NH_3)_2}}{\mathrm{Cl_2}}\right],$$

$$\left[\mathrm{Pt}\genfrac{}{}{0pt}{}{\mathrm{NH_3}}{\mathrm{Cl_3}}\right]\mathrm{K},\quad [\mathrm{Pt\,Cl_4}]\,\mathrm{K_2}$$

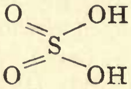
Hydrates

The application of Werner's theory to the study of hydrates is interesting.

When sulphur tri-oxide dissolves in water, it is assumed that a hydrate is first formed, owing to the oxygen of the water uniting with the sulphur by means of auxiliary valencies.

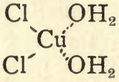
$$O_3S....OH_2$$

The mobility of the hydrogen ions now causes a rearrangement, whereby sulphuric acid

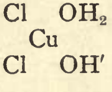


is produced.

In an analogous manner copper chloride may be supposed to combine with two molecules of water. Thus:



This molecule is capable of electrolytic dissociation, whereby the ions



$$\begin{matrix} Cl & & OH_2 \\ & Cu & \\ Cl & & OH' \end{matrix} \quad \text{and} \quad H^{\cdot}$$

are formed, and the solution reacts slightly acid. This explains the readiness with which basic salts are formed.

In such salts as zinc sulphate, $ZnSO_4 . 7H_2O$, and copper sulphate, $CuSO_4 . 5H_2O$, we have apparent exceptions to Werner's rule that the co-ordination numbers are either 4 or 6. Werner suggests, however, that in each case one molecule of water is attached to the sulphuric acid radicle. This certainly explains the greater difficulty experienced in expelling the last molecule of water.

As is well known, the alums contain twelve molecules of water, that is, twice the maximum co-ordination number.

XIX

ELECTROCHEMICAL THEORIES

THE theories which up to the present have engaged our attention have assumed that valency is merely an attractive force, not unlike that known as gravity. The most casual observer, however, cannot fail to be struck by the fact that the most stable compounds are formed by the union of elements of opposite electrical character, as for example potassium and chlorine. On the other hand, elements of similar character either do not combine at all, as in the case of chlorine and fluorine,[1] or they combine only with difficulty, as for example nitrogen and chlorine. It is not remarkable, therefore, that numerous attempts should have been made, from time to time, to account for chemical combination on electrochemical grounds.

Davy's Theory

In his Bakerian Lecture delivered on 20th November, 1806, Sir Humphry Davy[2] laid special emphasis on the close connection which he had observed to exist between electricity and chemical affinity. He pointed out that chemical attraction between two bodies could apparently be destroyed by imparting to one of them an electrical charge different from that which it was supposed to contain naturally. On the other hand, by imparting the same kind of charge, or, as Davy expresses it, by increasing its natural energy, the force of chemical attraction may be greatly intensified. For example, metallic zinc under ordinary conditions easily admits of oxidation. When negatively electrified, however, the reverse is true. Again, silver is difficultly oxidizable unless positively electrified.

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[1] Lebeau, *Compt. rend.*, 1906, **143**, 425.

[2] Davy, *Phil. Trans.*, 1807, p. 1.

If we have two bodies, the particles of which are in different electrical states, chemical combination may be expected to take place. The stability of the resulting compound will be the greater, the more perfectly balanced the electrical energies are. The change in properties will be correspondingly proportional. This is the simplest case of chemical union. It is usually found, however, that two different bodies have different degrees of the same electrical energy in relation to a third. For example, according to Davy, sulphuric acid has a greater attraction for lead than muriatic acid. Consequently, when two bodies, repellent to each other, act on a third body with different degrees of the same electrical attracting energy, that body possessing the weaker energy is repelled. This affords an explanation for what is known as elective affinity, and for the decompositions produced in consequence.

On the other hand, when two bodies have different degrees of the same energy with regard to a third body, and likewise different energies with regard to each other, there might be such a balance of attractive and repellent forces as to produce a triple compound. By following up this line of argument it is easy to see how more complicated structures may be accounted for.

Whenever bodies, raised by artificial means to exalted states of opposite electrification, are brought together, light and heat result. This was regarded as a confirmation of the above electrical theory of chemical affinity, for both light and heat result from intense chemical action. As in certain forms of the voltaic battery large quantities of electricity of low intensity are brought into action with the production of heat but no light, so in slow chemical combinations, a rise of temperature may be observed, unaccompanied by the emission of light. The effect of heat in producing chemical combination was supposed to be due to its increasing the motion of the particles, and raising their state of electrification.

The **Dualistic Theory** of Berzelius was essentially an electrochemical one. As we have already seen in an earlier chapter, every compound was, according to Berzelius, made up of two parts charged with electricity of opposite sign. This hypothesis was in harmony with the observation of Ritter,[1] that electricity originated with chemical decomposition.

Crum Brown's Hypothesis

In 1861, Crum Brown[2] suggested a theory of chemical combination which calls for consideration here. He assumed that each atom possesses two kinds of attractive force, which may be termed positive and negative respectively. The point towards which these forces act is known as the pole or active point. Monovalent elements such as hydrogen possess but one such pole; whilst oxygen would have two; and so on. When two atoms unite, an amount of the positive force of the one used up is equal to the amount of negative force employed in the other, and *vice versâ*.

The author did not regard these forces as electrical, for they were assumed to act at the same point at the same time, whereas electrical forces would wholly or partially neutralize each other. In all other respects, however, the forces exhibit an electrical nature, and for the sake of convenience in classification they may be regarded as due to charges of electricity situated on the atom indefinitely close to one another. When a divalent atom combines with two monovalent atoms, the forces in the former will be divided between its two poles, in a certain proportion depending on that in which the two forces exist in each of the two monovalent atoms. For example, consider the molecule of water, H_2O. The forces in the oxygen atom will be equally divided between the two hydrogen atoms, for there is no reason why one of these should appropriate more force than the other. If, however, we replace one atom of hydrogen by one of potassium—a body which possesses a greater amount of positive force—the same equal division will not take place. More of the negative force in the oxygen will accumulate at that pole which is next to the atom of potassium, and more of the positive force at the pole next to the remaining hydrogen atom. This latter will not now be so readily replaceable by positive atoms, as it was previously. On the other hand, it will be easily removed in favour of a negative radicle. In other words, we have here an explanation for the fact that its chemical relations have been modified by the properties of the potassium atom, although the latter is not in direct combination with it.

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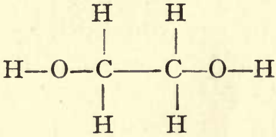
[1] Ritter, *Elektrisches System*, p. 49.

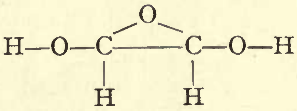
[2] Crum Brown, *On the Theory of Chemical Combination*, Edinburgh, 1861; first published, March, 1879.

By a similar process of reasoning an explanation is forthcoming for the fact that whereas glycol (to which Crum Brown gave the graphical formula identical with that employed to-day)



$$\begin{array}{ccccccc} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & \\ \mathrm{H}- & \mathrm{O}- & \mathrm{C} & - & \mathrm{C} & -\mathrm{O} & -\mathrm{H} \\ & & | & & | & & \\ & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

exhibits no acid properties, yet by replacing two atoms of hydrogen by one of oxygen, glycollic acid is obtained, to which the formula



was ascribed.

The negative force of the oxygen atom attracts the positive force in the carbon atoms towards itself in a greater measure. Consequently there will be an accumulation of negative force at the two poles opposite the two hydroxylic oxygen atoms. In order to balance this there will be an excess of positive force at the poles of these two oxygen atoms nearest to the carbon atoms, and an excess of negative force will be directed towards the two hydroxylic hydrogen atoms. These will therefore be more easily replaced by positive atoms than before, that is, than in glycol. Hence the body now reacts as an acid.

If, now, one of these hydrogen atoms be replaced by a positive atom, such as for example potassium, this will again alter the balance. There will be an accumulation of negative force at that active point turned towards the potassium, and the excess of negative force will be drained away, so to speak, from the one remaining hydroxylic hydrogen atom. Consequently this last-named atom loses its acid properties. Glycollic acid therefore reacts simply as a monobasic acid. In a similar manner explanations may be found for many other interesting observations.

As early as 1869, Blomstrand[1] pointed out that those elements, which are decidedly electropositive or electronegative, have the lowest saturation capacity. For example, if the halogens act decidedly negatively, their valency is always unity. Hence the generalization may be couched in the following manner:[2] *The intensity of electrochemical activity of an atom is inversely proportional to the numerical value of its valency.*

In his famous Faraday Lecture in 1881, Helmholtz revived the old idea that valency was the result of electrical forces. He boldly stated his conviction that there could be "no doubt that the very mightiest among the chemical forces are of electric origin. The atoms cling to their electric charges, and opposite charges cling to each other; but I do not suppose that other molecular forces are excluded, working directly from atom to atom."[3] . . . "If we conclude from the facts that every unit of affinity is charged with one equivalent either of positive or of negative electricity, they can form compounds, being electrically neutral only if every unit charged positively unites under the influence of a mighty electric attraction with another unit charged negatively. You see that this ought to produce compounds in which every unit of affinity of every atom is connected with one and only one other unit of another atom. This, as you will see immediately, is the modern chemical theory of quantivalence, comprising all the saturated compounds. The fact that even elementary substances, with few exceptions, have molecules composed of two atoms, makes it probable that even in these cases electric neutralization is produced by the combination of two atoms, each charged with its full electric equivalent, not by neutralization of every single unit of affinity."[1]

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[1] Blomstrand, *Chemie der Jetztzeit*, 1869, 217 and 243.

[2] Hinrichsen, *Zeit. phys. Chem.*, 1902, **39**, 305.

[3] Helmholtz, *Trans. Chem. Soc.*, 1881, **39**, 302–3.

During the past few years chemists and physicists have begun to consider valency from the point of view of Helmholtz. Our knowledge of the connection between matter and electricity has been so greatly extended, that the electrical nature of chemical affinity is regarded by many as certain. In 1901, in a lecture delivered at Hamburg, Nernst emphasized the views of Helmholtz in the words: "If, further, the most different elements or radicles invariably combine only with a definite quantity of free electricity, or with a multiple thereof, this can be most simply expressed by the statement: 'For compounds between ordinary matter and electricity, exactly the same fundamental chemical law holds as for compounds with each other of ordinary chemical substances, namely the law of constant and multiple proportions.' For example, if, in common salt, we replace the sodium atom by a negative electron, we obtain the negative chlorion; if we replace the chlorine atom by a positively charged electron, we obtain the positive sodium ion."

We are indebted to J. J. Thomson[2] and his pupils for much of our knowledge about electrons. Thomson has shown that, in the conduction of electricity through highly rarefied gases, the negatively charged particles, constituting the cathode rays, carry a charge identical with that conveyed by an atom of hydrogen or any other monovalent element, when acting as an ion in a solution. Further, the mass of these particles does not exceed one-thousandth of that of the hydrogen atom, neither is it changed by altering the substance supplying the particles. To these particles the name corpuscle has been given by Thomson, but the more commonly used name *electron* was devised by Johnstone Stoney.

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[1] Helmholtz, *Trans. Chem. Soc.*, 1881, **39**, p. 303.

[2] *Conduction of Electricity through Gases*, J. J. Thomson, 1903.

According to Lodge,[1] "Every electric charge is to be thought of as due to the possession of a number of electrons, but a fraction of an electron is at present considered impossible, meaning that no indication of any further subdivision has ever loomed even indistinctly above the horizon of practical or theoretical possibility. The electrification of an atom of matter consists in attaching such a unit to it, or in detaching one from it. An atom of matter with an electron in excess (or in defect) is called an ion."

Lodge[2] has also discussed the question of variable valency, and shows that it is not inconsistent with the supposed connection between electrons and chemical affinity.

"It has been," he writes, "an occasional habit with physicists when speaking of lines of force to think of a single line of attraction or elastic thread joining each negative electron to its corresponding positive charge; each unit charge, in fact, being regarded as the end of a line of force and nothing else. . . . But . . . there is no evidence that each unit of charge ought to have assigned to it one solitary line of force, it might have a great number; though it is true that on that view it becomes a definite question how many lines a unit charge possesses. On any view electrons are supposed to repel and to be attracted with a force varying as the inverse square of the distance, and this is only consistent with a very large number of lines of force radiating from each and starting out in every direction equally.

"When opposite charges have paired off in solitude, every one of these lines starts from one and terminates on the other constituent of the pair, and the bundle or field of lines constitutes a full chemical *bond;* but bring other charges or other pairs in the neighbourhood, and a few threads or feelers are at once available for partial adhesion in cross directions also. . . . The charge is indivisible, . . . but the lines of force emanating from it are not indivisible. . . . The bulk of them may be occupied with straightforward chemical affinity, while a few strands are operating elsewhere; and the subdivision of force may go on to any extent, giving rise to molecular combination and linking molecules into complex aggregates, etc."

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[1] Lodge, *Modern Views on Matter*, The Romanes Lecture, 1903.

[2] Lodge, *Nature*, 1904, **70**, 176.

This view is extremely interesting, for, as P. F. Frankland[1] points out, it shows the possibility of the existence of an indefinite number of different grades of chemical union, whereas, up to the present, only one such grade has been recognized. Thus, for example, in the dry state, sodium chloride may be looked upon as the union of one sodium atom with one of chlorine, effected by a Faraday tube or bundle. On dissolving the salt in water, however, some of the constituent fibres of the bundle become severed, with the result that the sodium and chlorine atoms become respectively combined with water. If excess of water be now added, all the fibres of the bundle may become severed and the connection between the atoms of sodium and chlorine is thus broken. The Faraday bundle, starting with its positive end on the sodium atom, will now terminate at its negative end in a number of fibres attached to different molecules of water. Similarly the bundle, beginning with its negative end on the chlorine atom, will now terminate at its positive end in a number of fibres likewise attached to different water molecules. In this way an explanation is forthcoming for the well-known fact that when common salt dissolves in water, it is dissociated into sodium and chlorine ions.

It is a little dangerous, however, to recognize the existence of so many different grades of chemical union. It is only by keeping the numerical value of the valency of the elements as small as possible that we are able, with any degree of certainty, to draw up graphical and constitutional formulæ for chemical compounds. Thus, for example, unless we limit the valencies of carbon and hydrogen to four and unity, respectively, a large number of graphical formulæ might be drawn up to represent such a simple substance as methyl iododichloride, CH_3ICl_2.[1] But the scheme

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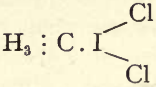
[1] Frankland, *Nature*, 1904, **70**, 223.



$$H_3 : C . I \begin{matrix} Cl \\ Cl \end{matrix}$$

is perfectly satisfactory.

W. Peters[2] points out that according to the electronic theory of chemical affinity, the forces acting between the atoms of a molecule are nearly independent of the masses of the atoms. Hence if two gases have the same number of atoms in equal volumes, and if they yield the same value for γ—the ratio of the specific heats at constant volume and pressure—then they possess the same molecular heat and internal energy at any fixed temperature. Consequently the total number of affinities acting between their atoms must be the same.

Thomson's Theory

According to J. J. Thomson[3] the atom consists of corpuscles moving in a sphere of uniform positive electrification. The mass of the atom is given by the sum of the masses of the corpuscles it contains.

The question therefore arises—How are the corpuscles arranged?

If constrained to move in one plane only, they must arrange themselves in a series of concentric rings. If, however, they are free to move in every direction, a series of concentric shells will be formed. A general solution for this latter case has not yet been arrived at. But the same kind of properties are associated with rings as with shells, and the author shows that the ring structure confers on the atoms properties which are analogous in many ways to those possessed by the chemical elements. In particular it is shown that the properties of the atom will depend upon the number of corpuscles it contains, that is, upon its atomic weight, in a way very analogous to that expressed by the Periodic Law.

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[1] Thiele and Peter, *Ber.*, 1905, **38**, 2842.

[2] Peters, *Zeit. Elektrochem.*, 1907, **13**, 657.

[3] Thomson, *Phil. Mag.*, 1904, (vi.) **7**, 237; 1906, (vi.) **11**, 769.

Thomson calculates that, if the atom consists of five concentric rings, then 59 is the smallest number of corpuscles which can have an outer ring of 20. When, however, the total number of corpuscles exceeds 67, the outer ring has more than 20. Consider the following series of arrangement, which indicates the number of corpuscles contained in successive rings, when the total number of corpuscles varies from 59 to 67. The outer rings all contain 20 corpuscles. In the first group the total number of corpuscles is 59, which is only just sufficient to impart stability to the outer ring. Hence, when the corpuscles are displaced, the forces of restitution urging them back to their original positions are small, and one or more corpuscles may easily be detached. By losing a corpuscle such an atom will become positively charged, and behave like an atom of an electropositive element.

Number of Corpuscles	59	60	61	62	63	64	65	66	67
No. in successive rings	20	20	20	20	20	20	20	20	20
	16	16	16	17	17	17	17	17	17
	13	13	13	13	13	13	14	14	15
	8	8	9	9	10	10	10	10	10
	2	3	3	3	3	4	4	5	5

Passing from group 59 to group 60, the outer ring becomes more stable, for the atom now contains an additional corpuscle. Consequently the atom is not so strongly electropositive as the preceding one. The addition of each successive corpuscle makes it more difficult to detach corpuscles from the outer ring, and the element becomes less electropositive. When the stability becomes very great, it may be possible for one or more corpuscles to lie on the surface of the atom without rupturing the ring. In this case the atom could receive a charge of negative electricity, and would behave as an atom of an electronegative element. This increase of stability would continue until we had a total of 67 corpuscles in the atom, and this is the condition of maximum stability for an outer ring of 20.

A great change in properties occurs if we have 68 corpuscles in the atom. The number in the outer ring now increases to 21, a condition which is on the verge of instability, and by readily losing a corpuscle, the system resembles the atom of a strongly electropositive element.

The properties of the 59- and 67-corpuscle atoms are very interesting, since these latter occur at the beginning and end of a series, which has 20 corpuscles in the outer ring. In group 59 the arrangement of corpuscles, though very near to the fringe of instability and therefore very liable to lose a corpuscle, would not be able to retain the positive charge thus acquired. For when it had lost a corpuscle, the 58 left would arrange themselves in the grouping corresponding to a 58-corpuscle atom, which is the last of a series containing 19 corpuscles in the outer ring. This ring is very stable, so that no more corpuscles could escape from it.

On the other hand, the positive charge on the system due to the escape of the 59th corpuscle would attract the neighbouring corpuscles. Hence the arrangement could not remain permanently charged, for as soon as one corpuscle had escaped it would be replaced by another. An atom constituted in this way would be neither electropositive nor electronegative; it would be incapable of receiving a permanent charge of electricity.

The group containing 60 corpuscles would be the most electropositive of the series. It can lose one corpuscle, but only one, for if it lost two, we should have a group of 58 corpuscles, similar to that obtained when one was removed from a 59-corpuscle atom, and such a system would be even more likely to attract external corpuscles, for it would have two units of positive electricity instead of one. Thus the 60-corpuscle system could be charged with one unit of positive electricity, but with no more. It would therefore act like the atom of a monovalent metal.

The group containing 61 corpuscles would not part with any of these as readily as a group of 60. It could, however afford to part with two, and it is not until it has lost three that its corpuscles are reduced to 58, and it begins to acquire fresh ones. It is clear, therefore, that the 61-corpuscle system might get charged with two units of positive electricity, and thus behave like the atom of a divalent metal.

Similarly group 62, though even less liable to lose corpuscles than group 61, may lose three without beginning to recover corpuscles. It would thus acquire a charge of three units of positive electricity, and act like the atom of a trivalent metal.

Let us now proceed to consider the system containing 67 corpuscles. The outer ring is very stable, and if it acquired an additional corpuscle rearrangement would take place, and an outer ring containing 21 corpuscles would be formed. As 68 is the smallest number of corpuscles which can exist under these circumstances with an outer ring of 21, it is clear that a corpuscle may easily be lost. The resulting group of 67, as soon as it acquired a negative charge in this way, would lose it again, and the system, like that containing 59 corpuscles, is thus seen to be incapable of receiving a permanent charge. It therefore acts like an atom of zero valency.

Group 66 would be the most electronegative of the series. It would, however, be only able to retain a charge of one unit of negative electricity, for if it acquired two, there would be 68 corpuscles, an arrangement which, as we have seen, readily loses corpuscles. This group of 66 would therefore act like the atom of a monovalent electronegative element.

Group 65 would be less liable than group 66 to acquire negative corpuscles. On the other hand, it might retain two additional corpuscles, and thus be charged with two units of negative electricity. Its properties would thus resemble those of a divalent electronegative element. Similarly group 64 would act like a trivalent electronegative element.

We thus have a series of nine groups, the first and last of which behave like atoms incapable of exerting valency. Proceeding in the order of increasing number of corpuscles we find systems corresponding to mono-, di-, and tri-valent electropositive elements, and, at the other end, systems corresponding to tri-, di-, and mono-valent electronegative elements. This is similar to the Periodic Classification :

He	Li	Be	B	C	N	O	F	Ne
Ne	Na	Mg	Al	Si	P	S	Cl	A

and so on.

When atoms with very stable outer rings are mixed with others, the corpuscles of which are not so firmly attached, a transference of corpuscles may take place. The electronegative atoms will thus receive a negative charge, and the electropositive atoms a positive charge. These oppositely charged atoms will attract one another, and a chemical compound will be formed.

Abegg's Theory

Abegg and Bodländer[1] and Abegg[2] have worked out a very complete theory, according to which every element possesses two kinds of valency, namely Normal and Contravalency. These are of opposite polarity, but the former is regarded as the stronger, and corresponds to the usually accepted valencies of the elements.

In the case of the metals the normal valencies are positive, but negative in the non-metals. The total sum of the valencies is, in every case, eight, for

Normal Valencies = 8 − Contravalencies.

The following table, based on the Periodic Classification, shows how these valencies are distributed amongst the elements :—

Valencies.	Groups.						
	1.	2.	3.	4.	5.	6.	7.
normal	+1	+2	+3		−3	−2	−1
				±4			
contra	−7	−6	−5		+5	+6	+7

It frequently happens that all the normal valencies are not exerted, and the contravalencies may likewise remain latent.

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[1] Abegg and Bodländer, *Zeit. anorg. Chem.*, 1899, **20**, 453.

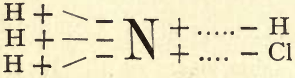
[2] Abegg, *Zeit. anorg. Chem.*, 1904, **39**, 330.

The latter, however, increase in activity as the atomic weight rises, as is well shown in the case of the halogens. Whilst fluorine with an atomic weight of 19 is unable to combine with oxygen, iodine with an atomic weight nearly seven times as great gives a very stable oxide.

It is well known that metallic molecules are almost exclusively monatomic when in the vaporous state. Non-metallic molecules, on the other hand, are usually polyatomic, owing to the activity of their contravalencies.

The actual strength of the several normal valencies of any one element is regarded as the same before actual combination, but saturation of any one of them weakens the rest. This affords an explanation for the fact that the valency which any particular element exhibits depends on the character of the atom or group to which it is attached. For example, the highest chloride of arsenic has the formula $AsCl_3$, but towards fluorine arsenic can function as a pentavalent atom, for Ruff and Graf[1] have succeeded in isolating the pentafluoride, AsF_5. Attention is called to the so-called amphoteric elements,[2] such as sulphur, nitrogen, and arsenic, which can exert positive and negative affinities, but not both at the same time.

Ammonium chloride may be represented by the scheme



where the contravalencies are represented by dotted lines. Since the fourth hydrogen atom is here attached by its weak contravalence an explanation is forthcoming for the fact that ammonium chloride readily dissociates on heating. As we have already seen,[3] however, there is every reason to believe that the four hydrogen atoms in ammonium chloride are equivalent, and that no such difference as that indicated by Abegg's formula in reality exists.

Association is attributed to the existence of unsaturated valencies in at least one of the constituent atoms. We might therefore expect such molecules to contain one or more elements belonging to the higher groups in the Periodic System. This is frequently found to be the case, as for example, the molecules of water, H_2O, nitrogen peroxide, N_2O_4, hydrofluoric acid, H_2F_2, etc. For a similar reason we should anticipate that these elements would play an important part in the formation of the so-called molecular compounds. Nor are we disappointed, for the alums, double chlorides, ammoniates, and alcoholates are cases in point. The advantage of this theory is that we do not need to postulate the existence of indefinite crystallographic forces to account for the formation of these complexes.

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[1] Ruff and Graf, *Ber.*, 1906, **39**, 67.

[2] Abegg, *op. cit.*, p. 340.

[3] See page 85.

The application of Abegg's theory to the study of solutions is of special interest. When the solution of a substance in a liquid is accompanied by change of temperature, it is assumed that combination has taken place between solute and solvent. When both of these contain elements of high, but not completely saturated, valency, the effect is most conspicuous. The solute will tend to prevent the association of the solvent, and *vice versâ*.

In electrolytic solutions we therefore have the following equilibria:—

(1) Undissociated molecules $\rightleftharpoons$ ion + ion.

(2) Undissociated molecule + solvent $\rightleftharpoons$ compound of undissociated molecule and solvent.

(3) Solvent + ion $\rightleftharpoons$ compound of ion and solvent.

When salts dissolve in water, there is but little tendency for (2) to take place, since (1) is well developed, and the salt is almost entirely ionised.

Spiegel and Arrhenius

In 1902, Spiegel[1] suggested that certain elements possess what he terms *neutral affinities*, that is, valencies which can be called out in pairs of equal and opposite sign, and which, when not externally saturated, neutralize one another. They exert, therefore, no action on the electrochemical character of the element.

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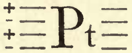
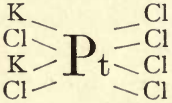
[1] Spiegel, *Zeit. anorg. Chem.*, 1902, **29**, 365.

In ammonia, NH_3, three valencies of nitrogen are active, and in water, H_2O, two of oxygen. In the ammonium and oxonium salts, however, neutral affinities are called out. The power of exerting neutral affinities is not confined to nitrogen and oxygen. Other elements may possess them, as for example platinum, the atom of which may be schematically represented as



On the right, the four active valencies are shown. On the left, two pairs of neutral affinities. Potassium platinichloride, K_2PtCl_6, has therefore the graphical formula



The *co-ordinate numbers* of Werner thus become the sum of the active and neutral valencies.

The subject has not been worked out in any detail, but further contributions are promised.

Arrhenius[1] has given expression to very similar views. His *electrical double valencies* correspond to Spiegel's neutral affinities, but his theory has not been so fully worked out.

Ramsay's Theory

A great advance in the electrical conception of valency has recently been made by Ramsay.[2] In his Presidential Address to the Chemical Society in March, 1908, he suggested the following hypothesis :—

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[1] Arrhenius, *Theorien der Chemie*, Leipzig, 1906.

[2] Ramsay, *Trans. Chem. Soc.*, 1908, **93**, 778.

"Electrons are atoms of the chemical element, electricity; they possess mass; they form compounds with other elements; they are known in the free state, that is, as molecules; they serve as the 'bonds of union' between atom and atom."

To the electron Ramsay assigns the symbol E. When common salt dissolves in water it becomes ionized. The sodium now carries a positive charge, and the chlorine an equal negative charge. In other words, the sodium ion, or "sodion," is an atom of sodium minus an electron, and the chlorine ion, or "chlorion," is an atom of chlorine plus an electron. The sodium atom may therefore be regarded as a compound of the element sodion with an electron, whilst, on the other hand, the chlorion is a compound of an electron with an atom of chlorine.

The metal sodium readily combines with chlorine, as every chemist is aware, with the production of common salt. If, for the sake of simplicity, we regard the chlorine molecule as already split up into atoms before the introduction of the sodium, the equation representing this change may be written as

$$\mathrm{ENa} + \mathrm{Cl} = \mathrm{NaECl}.$$

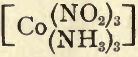
Here the electron, E, serves to unite the atom of sodium to the atom of chlorine. In other words, it is the electrical interpretation of that connecting force known as valency.

In order to form a mental picture of what occurs, Ramsay suggests that an electron may be regarded as an amœboid structure which surrounds a positive ion, converting it into an atom. The atom ENa may therefore "be conceived of as an orange of sodium surrounded by a rind of electron." When, however, combination between the sodium and chlorine atoms takes place, the electron collects on one side of the sodium atom, and forms a cushion between it and the chlorine, thus: NaECl.

Now, suppose we consider two atoms of the same element, for example, chlorine. Here we have, apparently, two atoms joined together without an electron. But such is not really the case. In ClO_2, $KClO_3$, and $KClO_4$, chlorine is evidently functioning as a polyvalent atom. In other words, it has a store of electrons. In potassium perchlorate it may be regarded as heptavalent, so that it can dispose of at least seven electrons. The molecule Cl_2 may therefore be written $E_6ClEClE_7$, etc. Of course this is far too cumbersome, and in our ordinary formulæ we can afford to ignore the latent electrons and make use of those only which are of service for the moment.

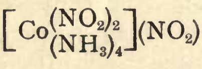
When ammonium chloride is dissolved in water, it is dissociated into $NH_4^{\cdot}$ and Cl' ions. We may therefore regard its molecule as NH_4ECl. On solution in water, E remains attached to the chlorine atom, converting it into an ion. We may suppose that the nitrogen atom itself carries five electrons, and receives three more from the three hydrogen atoms in ammonia, NH_3. This makes the grand total of eight, which is regarded as the maximum possible. If therefore, we try and add one more, as in NH_4, this is impossible, unless the nitrogen can part with one to a negative ion such as chlorine.

We must now pass on to consider the nature of Werner's complexes, in the light of Ramsay's theory. As a typical example we may take the nitrites of the cobaltammines, which possess the peculiarity of being non-ionized, or partially or completely ionized, according to the number of ammonia groups present. Thus, whilst

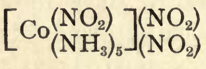


$$\left[\mathrm{Co}^{(NO_2)_3}_{(NH_3)_3}\right]$$

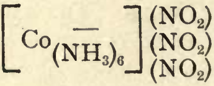
is non-ionized, the complexes



$$\left[\mathrm{Co}^{(NO_2)_2}_{(NH_3)_4}\right](NO_2)$$

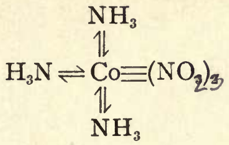


$$\left[\mathrm{Co}^{(NO_2)}_{(NH_3)_5}\right]\begin{matrix}(NO_2)\\(NO_2)\end{matrix}$$



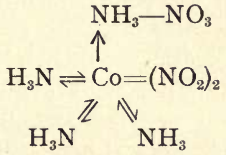
$$\left[\mathrm{Co}^{\;-\!-}_{(NH_3)_6}\right]\begin{matrix}(NO_2)\\(NO_2)\\(NO_2)\end{matrix}$$

contain one, two, and three NO_2 ions respectively. We have already seen that, according to Ramsay's theory, the nitrogen in ammonium chloride takes one electron from the fourth atom of hydrogen, and parts with one to the chlorine. In a similar manner each nitrogen atom in ammonia groups of the cobaltammines may be regarded as receiving one electron from the cobalt, and giving one at the same time. The formula for the undissociated tri-ammino-nitrite is therefore



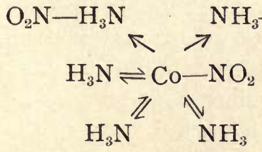
$$\begin{array}{c} \mathrm{NH_3} \\ \upharpoonleft\downharpoonright \\ \mathrm{H_3N} \rightleftharpoons \mathrm{Co} \equiv (\mathrm{NO_2})_3 \\ \upharpoonleft\downharpoonright \\ \mathrm{NH_3} \end{array}$$

If a fourth NH_3 group is now added, the cobalt atom gives an electron to the nitrogen, but does not receive one in return. The nitrogen is therefore "overloaded," for it has received four electrons in addition to the normal five, which makes nine in all. As elements are apparently incapable of being associated with more than eight electrons, the nitrogen must lose one. This it does by imparting one to an NO_2 group, which now parts company with the cobalt atom, and becomes ionizable on solution in water, since a complex ammonium nitrite has thus been formed. The following scheme will make this clear:—



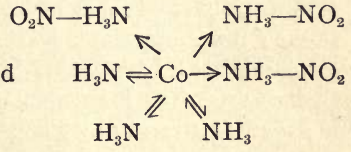
$$\begin{array}{c} \mathrm{NH_3{-}NO_3} \\ \uparrow \\ \mathrm{H_3N} \rightleftharpoons \mathrm{Co} = (\mathrm{NO_2})_2 \\ \swarrow\!\!\nearrow \quad \searrow\!\!\nwarrow \\ \mathrm{H_3N} \qquad \mathrm{NH_3} \end{array}$$

The remaining formulæ may be written similarly



$$\begin{array}{c} \mathrm{O_2N{-}H_3N} \qquad\qquad \mathrm{NH_3{-}NO_2} \\ \nwarrow \quad \nearrow \\ \mathrm{H_3N} \rightleftharpoons \mathrm{Co{-}NO_2} \\ \swarrow\!\!\nearrow \quad \searrow\!\!\nwarrow \\ \mathrm{H_3N} \qquad \mathrm{NH_3} \end{array}$$

and



$$\begin{array}{c} \mathrm{O_2N{-}H_3N} \qquad\qquad \mathrm{NH_3{-}NO_2} \\ \nwarrow \quad \nearrow \\ \mathrm{H_3N} \rightleftharpoons \mathrm{Co} \rightarrow \mathrm{NH_3{-}NO_2} \\ \swarrow\!\!\nearrow \quad \searrow\!\!\nwarrow \\ \mathrm{H_3N} \qquad \mathrm{NH_3} \end{array}$$

We have now to find an explanation for the undissociable nature of the complex $Co(NO_2)_3(NH_3)_3$. The metal cobalt may be regarded as having three electrons associated with it; in other words, metallic cobalt is really cobalt tri-electride. In the ionic condition it has parted with its electrons. A glance at the schemes given above shows that in the hexammino-complex, however, the cobalt has not got three electrons at disposal. It has parted with them to the $NH_3 . NO_2$ groups. We are thus led to the conclusion that, in the non-ionizable compound, the cobalt does not, as in its ordinary salts, part with three electrons, but it receives them from the nitro-groups. Why the presence of some one substituting element or group in a compound should influence the position into which a second substituting element or group shall enter, it is difficult to see. Possibly an explanation is to be found in the varying electronic affinity exhibited by radicles already occupying a position in a compound.

Friend's Theory

Friend[1] distinguishes three kinds of valency.

1. *Free negative valency.*

Since hydrogen is electropositive and monovalent, only those elements which possess a negative valence can combine with it. As Ramsay has pointed out, this is equivalent to saying that only those elements which are capable of receiving electrons can form hydrides. It is interesting to note that no duly authenticated compounds are on record containing hydrogen attached to one atom of any other element in two or more proportions. Thus, whilst hydrogen phosphide, PH_3, and methane, CH_4, are easily prepared, the radicles phosphonium, PH_4, and methyl, CH_3, have resisted all attempts at isolation.

As we have seen in an earlier chapter, there is evidence to show that ammonium, NH_4, can exist as an amalgam with mercury; but it is not possible to prepare it in the free state. In the case of all the non-metals, therefore, hydrides may be regarded as trustworthy guides to the numerical value of the free negative valencies of the element—in other words, to the number of electrons with which that element can combine.

2. *Free positive valency.*

In addition to negative, some elements possess positive valency, that is to say, they are also able to part with electrons.

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[1] Friend, *Trans. Chem. Soc.*, 1908, **93**, 260.

Such elements may be termed *amphoteric*.[1] Others apparently possess only positive or only negative valency.

The numerical value of the positive valency is not so easily determined as that of the negative, since we have no negative element corresponding with hydrogen, which combines with one atom of any other element in only one proportion. Abegg adopts the suggestion of Mendeléeff,[2] and assumes that the highest oxygen compounds, omitting peroxides, give the maximal valency of the elements. Not only is this method somewhat uncertain owing to the divalent nature of oxygen, but it is inconsistent. The valency of manganese, for example, is decided by a much higher and more unstable oxide than the peroxide, namely the heptoxide, Mn_2O_7. Friend therefore suggests that fluorine is the most suitable element for determining the maximum positive valency of the elements.

Martin[3] has already drawn attention to the similarity of oxygen and fluorine, and the latter possesses the decided advantage of being monovalent.

Chlorine, fluorine, and oxygen are the only elements which possess free negative but no free positive valencies. Metals apparently possess free positive valencies alone. A list of all the amphoteric elements, together with their fluorides and hydrides, is given in the adjoining table. The fact that in the majority of cases the sum of the free valencies is eight is very remarkable. Some chemists assume that every element possesses eight valencies.[4] It is difficult to believe, however, that such is true in the case of hydrogen, the inert gases, and the alkali metals—to take extreme examples. Although no fluoride of nitrogen has hitherto been discovered, yet nitrogen is regarded as amphoteric on account of the stability of its oxides and oxyfluorides.

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[1] Abegg, *Zeit. anorg. Chem.*, 1904, **39**, 340.

[2] Mendeléeff, Ostwald's *Klassiker*, **68**, 48.

[3] Martin, *Chem. News*, 1904, **89**, 49.

[4] Abegg, *Zeit. anorg. Chem.*, 1904, **39**, 340; Morozoff, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, ii. 481.

TABLE OF AMPHOTERIC ELEMENTS.

Element.	Hydride.	Free negative valency.	Fluoride.	Free positive valency.	Total free valency.
Antimony . .	SbH_3	3	SbF_5[1]	5	8
Arsenic . . .	AsH_3	3	AsF_5[2]	5	8
Boron . . .	BH_3	3	BF_3[3]	3	6
Bromine . . .	BrH	1	BrF_3[4]	3	4
Carbon . . .	CH_4	4	CF_4[5]	4	8
Iodine . . .	IH	1	IF_5[6]	5	6
Nitrogen . .	NH_3	3	NOF[7]	3	6
Phosphorus . .	PH_3	3	PF_5[8]	5	8
Selenium . .	SeH_2	2	SeF_6[9]	6	8
Silicon . . .	SiH_4	4	SiF_4[10]	4	8
Sulphur . . .	SH_2	2	SF_6[11]	6	8
Tellurium . .	TeH_2	2	TeF_6[9]	6	8

3. *Residual or latent valency.*

By latent valency Friend understands positive and negative valencies, which differ from the above-mentioned free valencies in that *they can only be called out in pairs of equal and opposite sign.*

In Ramsay's phraseology, this is equivalent to saying that when an element exerts its latent valency, it simultaneously parts with, and receives, an electron. Consequently the sum-total of the electrons remains the same, and the electrochemical properties of the atom are unaltered. In this respect the latent valencies resemble the *neutral affinities* of Spiegel, and the *electrical double valencies* of Arrhenius. The molecule of hydrogen may therefore be represented as

$$\mathrm{H}\begin{smallmatrix}+ & \rule{2em}{0.4pt} & -\\ - & \rule{2em}{0.4pt} & +\end{smallmatrix}\mathrm{H} \quad \text{or} \quad \mathrm{H}\rightleftarrows\mathrm{H}$$

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[1] Ruff and Plato, *Ber.*, 1904, **37**, 673.

[2] Ruff and Graf, *Ber.*, 1906, **39**, 67.

[3] Gay Lussac and Thenard, *Ann. Chim. Phys.*, 1809, **69**, 204.

[4] Prideaux, *Proc. Chem. Soc.*, 1905, **21**, 240.

[5] Moissan, *Compt. rend.*, 1890, **110**, 276 and 951.

[6] Gore, *Chem. News*, 1871, **24**, 291.

[7] Ruff and Stäuber, *Zeit. anorg. Chem.*, 1905, **47**, 190.

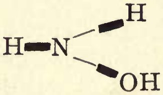
[8] Thorpe, *Annalen*, 1876, **182**, 201.

[9] Prideaux, *Trans. Chem. Soc.*, 1906, **89**, 316.

[10] Gay Lussac and Thenard, Gilbert's *Annalen*, 1809, **32**, 1.

[11] Moissan and Lebeau, *Compt. rend.*, 1900, **130**, 865.

in which latter scheme the arrows indicate the directions in which the electrons pass. In order to distinguish between free and latent valencies, it is suggested that the former be represented by thicker lines, as in hydroxylamine (below). It is not necessary for all the free valencies to be saturated before the latent valencies are called out. In a molecule of hydrogen, for example, no free valencies are saturated, and in hydroxylamine



two negative valencies remain unsaturated. That is, in the former case, each hydrogen atom is still capable of parting with an electron, and in the latter case, the nitrogen is open to receive two electrons. In the metallic hydrides combination is presumably effected by latent valencies, for example potassium hydride

$$\cdot \mathrm{K}{=}\mathrm{H} \cdot$$

We may assume that the addition and removal of electrons take place at definite points on a spherical surface representing the atom. Consequently, when an atom exerts its latent valencies, it parts with an electron from one point, and simultaneously receives another from a second point. The activity of the latent valencies depends upon the distance δ (Fig. 5) through which the electrons have to travel, and this is determined by two factors:

1. The radius of the atomic sphere.

Let r be the radius of the sphere, and θ the angle subtended at its centre by the arc between the points of electronic activity. Since two spheres can only meet at one point, δ varies with the size of the atoms. If these are equal, and θ is small and constant, δ will also be comparatively small, and the two atoms will be strongly attracted. This is true for the molecules of oxygen, hydrogen, etc., which are very stable.

If the temperature is raised, in the case of heavy atoms, the increased momentum, caused by the more rapid motion, may suffice to separate them, and the molecules will thus become monatomic. Iodine furnishes us with a good example of this.

If θ approximates to 60°, δ can only be made very small by introducing three atoms into the molecule. On the other hand, the weight of the molecule has now been increased, and this is conducive to instability. Oxygen is a case in point. Its diatomic molecule is very stable, but ozone is readily decomposed on warming.

If two atoms of different sizes are brought together, δ may be large, even though θ remain constant. The resulting compound will be then unstable. In this way an explanation may be found for the fact that, though the atoms of hydrogen in the molecule H_2 are firmly bound together, yet when bound by latent valencies to the larger atoms of the metals, the combination is weak.

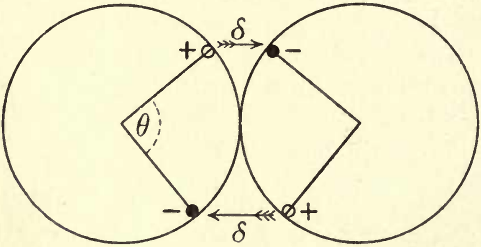


FIG. 5.

2. The angle θ.

θ probably varies for different elements. As θ increases, δ increases, and the stability of the diatomic molecules decreases. This probably explains why the metals are almost exclusively monatomic in the vaporous condition. In the case of the inert gases which possess no free valency, θ probably approximates to 180°, and diatomic molecules would thus be very unstable. As δ can only be made smaller by increasing the number of atoms in the molecule, a procedure which would render the latter unstable by reason of their weight, the molecules remain monatomic.

Metals

The study of the valency of the metals generally has proved very puzzling. In the vapour state they are chiefly monatomic,[1] nevertheless many alloys are known in the liquid and solid state. It is clear, therefore, that their latent valencies are weak. This is supported still further by the researches of Ramsay and of Tammann, the latter of whom has drawn attention to the fact that nearly all metals consist of monatomic molecules in mercurial solutions, even at temperatures as low as $-40°$ C.[2]

Tammann further points out that the valencies of the metals, as exhibited in their alloys, do not agree with those exhibited in their salts. Out of one hundred alloys, the formulæ of only twenty-six agreed with the ordinary valencies attributed to the metals, and this agreement he regards as largely due to accident.

This is well illustrated, to select a recent example, by the work of Gwyer.[3] This investigator employed Tammann's method of thermal analysis, controlled by microscopic observations, and was able to demonstrate the existence of the following compounds: $CuAl_2$, $CuAl$, Cu_3Al; $NiAl_3$, $NiAl_2$, $NiAl$; Co_3Al_{13}, Co_2Al_5, $CoAl$. Scores of other investigations illustrate the same fact, but it is superfluous to record them here.

According to Friend's theory, however, this is precisely what we might expect, for in the salts the metals are combined by means of their free valencies, but in the alloys, usually by their latent valencies only.

In the paper already referred to, Tammann states that the alloys of antimony are exceptional, as these exhibit valencies corresponding most closely with those usually attributed to the metal. This is easy to understand, for, as we have already seen, antimony is an amphoteric element. Hence when combining with metals it behaves as a non-metal by exerting its free negative valencies, and the metals are thus attached to it by their free positive valencies, and not by their latent valencies. From the above it will be clear that a metal may be defined as *an element which possesses, in addition to latent valencies, free positive valencies only ;* or, in Ramsay's phraseology, a metal is *an element which has no great affinity for electrons.*

---

[1] Wartenberg, *Zeit. anorg. Chem.*, 1907, **56**, 560; see also Kurbatoff, *J. Russ. Phys. Chem. Soc.*, 1907, **39**, 1181 and 1216; and others.

[2] Ramsay, *Trans. Chem. Soc.*, 1889, **55**, 521; Tammann, *Zeit. anorg. Chem.*, 1907, **55**, 289.

[3] Gwyer, *Zeit. anorg. Chem.*, 1908, **57**, 153.

Fluorine

Since all endeavours to obtain oxides of fluorine have proved unavailing, it is assumed that fluorine possesses no free positive valencies. Brauner[1] assumed that its remarkable chemical activity was due to its molecules being monatomic. Moissan,[2] therefore, re-determined the density of fluorine, using Regnault's method. As the mean of four determinations, he obtained the value 1·31, instead of the theoretical 1·316, which is sufficiently near to make Brauner's assumption inadmissible.

Friend suggests that **the activity of fluorine is due to its monovalent nature, and the entire absence of free positive valencies.** This explains the analogy between oxygen and fluorine, to which Martin[3] has called attention.

Nitrogen

The study of the valency of nitrogen is one of particular interest, for the number of inorganic and organic bodies, of which this element is a constituent, is exceeding great.

Although Ruff and Geisel[4] showed that no fluoride of nitrogen was capable of existing under ordinary conditions, yet the stability of its oxides and oxyfluorides shows that nitrogen possesses free positive valencies. What the numerical value of these valencies may be, is less easy to determine, but the author regards them as three in number.

In ammonia, NH_3, the three negative valencies of nitrogen are saturated. It is clear that a fourth cannot be called out, unless it is accompanied by an equal positive valence. This explains why all attempts to isolate ammonium have proved futile, for the only possible way in which it could be formed is by the fourth atom of hydrogen attaching itself to the nitrogen by means of latent valencies. Thus :

---

[1] Brauner, *Zeit. anorg. Chem.*, 1894, **7**, 12.

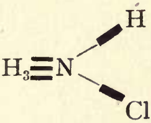
[2] Moissan, *Compt. rend.*, 1904, **138**, 728.

[3] Martin, *Chem. News*, 1904, **89**, 49.

[4] Ruff and Geisel, *Ber.*, 1903, **36**, 2677.

$$H_3\equiv N=H\cdot$$

If, however, the positive latent valence can be saturated by a fifth atom of an electronegative element, the problem is solved. For example, ammonium chloride may be represented by the formula



When we remember the ease with which ammonium chloride dissociates, and the great stability of hydrochloric acid, it seems highly probable that, when this latter substance and ammonia first come into contact, the compound

$$H_3\equiv N=Cl-H$$

is formed, which then undergoes rearrangement, until equilibrium is reached between the two tautomers. This lends support to Cain's formula, namely $H_3N:ClH$.[1] An explanation is thus forthcoming for the fact that, although perfectly dry ammonia and hydrochloric acid will not unite, combination readily takes place if a trace of benzene vapour is added. The last-named substance simply serves to bring the molecules together, an ionising body, such as water, not being necessary.

The oxides of nitrogen form a very interesting study from the point of view of valency. The remarkable inertness of the nitrogen molecule is probably due to the fact that the three positive valencies of one atom are completely saturated by the three negative valencies of the other. Thus :

$$N\begin{smallmatrix}+\\+\\+\end{smallmatrix}\equiv\begin{smallmatrix}-\\-\\-\end{smallmatrix}N$$

---

[1] Cain, *Mem. Manchester Phil. Soc.*, 1904, **48**, xiv.

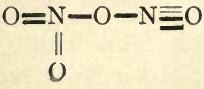
It will be observed that nitrogen is the only gaseous element in which such combination is possible, for it is the only one which has an equal number of free positive and negative valencies. We have already mentioned that the free positive valencies of nitrogen cannot be called out when one, two, or three of its free negative valencies are saturated, and *vice versâ*. Consequently, in the molecule of nitrogen, neither atom is capable of exerting its free valencies until the triple link has been ruptured. This would evidently be more difficult to accomplish than the separation of atoms joined merely by latent valencies, as in case of the hydrogen molecule, for example. The inert nature of the nitrogen molecule is therefore a property to be expected, rather than otherwise. When, however, the molecule has once been ruptured, we might expect nitrogen, on account of its amphoteric nature, to be capable of forming a large number of compounds, and our expectations are realized. The rupture of the molecule may be effected by passing a stream of electric sparks through a mixture of nitrogen and oxygen gases. Nitric oxide, NO, is one of the products. This is a remarkable gas, for it is most probably *the only example of tetravalent nitrogen*. Its formula is

$$\cdot N{\equiv}O$$

That the two latent valencies of nitrogen saturate the two of oxygen is clear from the fact that the molecules of nitric oxide remain single at temperatures as low as −100° C. Were the case otherwise, association to double molecules would be caused either by the activity of the oxygen, or by that of the nitrogen. Thus:

$$\cdot N{=}O{=}O{=}N\cdot \quad \text{or} \quad O{=}\dot{N}{=}\dot{N}{=}O$$

When, however, a molecule of oxygen is brought into contact with several of nitric oxide, the unsaturated nature of the latter is shown by the immediate production of nitrogen peroxide, to which the formula



$$\begin{array}{l} O{=}N{-}O{-}N{\equiv}O \\ \quad\ \ \| \\ \quad\ \ O \end{array}$$

may be given. That the molecule of oxygen has been ruptured and not merely added as a whole to the nitric oxide is proved by the fact that when heated, nitrogen peroxide dissociates, not into nitric oxide and oxygen at once, but first into single molecules of NO_2.

In an earlier chapter we have seen that the directions in which the valencies of the trivalent nitrogen atom act, very probably lie in one plane. If the atom is regarded as spherical, the three electrons may be assumed to lie at equal distances from one another on the circumference of a great circle of the sphere. When the latent valencies are called out whereby the nitrogen behaves as a pentavalent atom, rearrangement takes place. The four electrons constituting the four negative valencies will lie on the circumference of a great circle at equal distances from one another. The fifth, a positive valence, is caused by the escape of an electron from either one of the two poles of the sphere (Fig. 6).

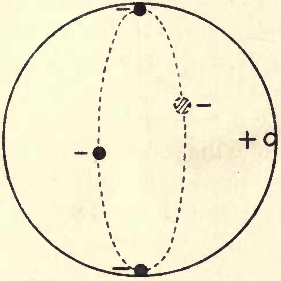


FIG. 6.

Complex salts

As we have already seen in an earlier chapter,[1] two compounds are known having the composition $PtCl_4(NH_3)_2$. Neither isomer shows any appreciable dissociation in aqueous solution. According to Friend,[2] the chlorine and ammonia form a shell round the metal in the way indicated by Werner. They are, however, joined together by latent valencies, but are not necessarily attached to the metal itself. Thus, the formula becomes[1]

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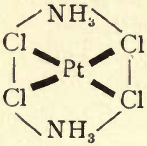
[1] See Chapter XVIII.

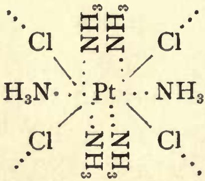
[2] Friend, *Trans. Chem. Soc.*, 1908, 93, 1006.



Whilst possessing none of the disadvantages of the formulæ of Werner and Spiegel, this scheme affords a ready explanation for the fact that dissociation cannot take place without the destruction of the complex.

If, now, the four chlorine atoms in the ring are replaced by ammonia, the complex $[Pt(NH_3)_6]Cl_4$ is obtained. According to Werner, the six NH_3 groups are attached directly to the platinum, and constitute the first zone. The dissociable chlorine atoms hover around the nucleus in an indefinite manner, and constitute the second or outer zone.

Spiegel has not given a formula for this body. Briggs[2] assumes that every element has two kinds of affinity, and suggests the formula:

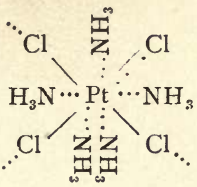


in which the unbroken lines represent the positive affinities of the platinum, and the dotted lines, the negative affinities. By removing a molecule of ammonia, and saturating the negative affinity of the platinum thus liberated by the free positive affinity of one of the chlorine atoms, we obtain the formula

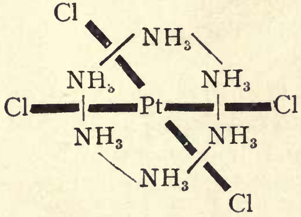
---

[1] For the sake of clearness the atoms are here, and in the succeeding schemes, represented as lying in one plane. It is easy to see that if a second pair of latent valencies is called out from each atom in the ring, a spatial configuration is obtained.

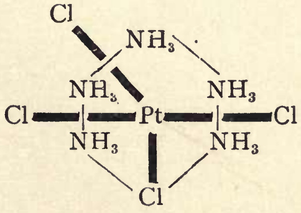
[2] Briggs, *Proc. Chem. Soc.*, 1908, **24**, 94; *Trans. Chem. Soc.*, 1908, **93**, 1564.



According to Friend, the former complex is represented by the scheme

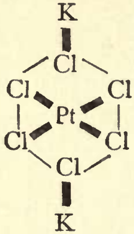


in which the platinum retains its tetravalent nature. The dissociability of the chlorine atoms is due, therefore, to *their being attached to the platinum atom, but not being included in the shell.* It is easy to see, by this arrangement, that the complex $[Pt(NH_3)_6]$ will form an ion, for the platinum atom will be unable to escape from the hexatomic nitrogen shell surrounding it. The formula for the complex $\left[Pt^{(NH_3)_5}_{Cl}\right]Cl_3$ will thus be



in which one chlorine atom has been included in the shell. Consequently only three chlorine atoms are dissociable.

In potassium platinichloride, K_2PtCl_6, we have a typical example of a second class of complex salts, namely that in which the simple ions are positive, and are directly attached to the shell, and not to the metallic atom. Thus:



By working along lines similar to these, it is easy to construct suitable formulæ for all the complexes which have as yet been discovered.

It is interesting to observe that inorganic compounds may thus be grouped into two classes, namely, those which contain hexatomic shells and those which do not; whereas organic compounds are classified according as they possess hexatomic rings or not.

XX

THE PHYSICAL CAUSE AND NATURE OF VALENCY

EXCEPT in Chapter XIX. we have hitherto generally made the tacit assumption that atoms possess a definite attractive force called valency, and have based on this the study of chemical combination. This is really all that concerns the chemist, for researches into the nature of the physical cause and nature of valency belong, properly speaking, to the physicist.

In order to deal fully with all the various theories which have been proposed from time to time, it would be necessary to consider the different views which have been advanced with regard to the nature of the atom, and far more space would be required than we have at our disposal here. We must therefore be satisfied by giving a rough outline of one or two of the more important theories, other than those based on electrical considerations which have been fully dealt with in the previous chapter.

Ensrud's Theory

According to Ensrud,[1] an atom consists of a shell of small density enclosing a nucleus of great density. Between the nuclei of different atoms attractive forces exist; between their envelopes, however, the forces are repellent. The nucleus is supposed to be excentric, and the smallest distance between the nuclei of two atoms is the direction in which the valency acts. If an atom has several nuclei, the valency may act in several directions; in other words, the atom is polyvalent, the maximum valency being determined by the number of nuclei within the shell.

---

[1] Ensrud, *Zeit. phys. Chem.*, 1907, **58**, 257.

Le Bas[1] has found that valency may be connected with the amount of energy in the molecule, and illustrates this view with the aid of the heats of combustion of the hydrocarbons. It is pointed out that—

The molecular heats of combustion of the hydrocarbons are proportional to their valency numbers.

Isidor Traube[2] points out that a constant is obtained by dividing Brühl's values for the molecular refractions of several homologous series of saturated carbon compounds by the total number of valencies present in the molecule. This constant is termed the refraction stere. Abnormal values are obtained for compounds, such as methyl alcohol, which readily associate. Compounds with an equal number of valencies, for example propyl alcohol and propionic acid, exhibit the same molecular refraction. This, therefore, affords a method of determining the valency of an element in certain of its compounds. It is interesting to note that oxygen exhibits, according to this theory, a valency of two, except in certain associated liquids, when it appears to be tetravalent.

The Theory of Barlow and Pope

In a series of very interesting papers, Sollas[3] has greatly extended our knowledge of the intimate structure of crystals. The volume of space appropriated by an atom is regarded as having the form of a solid of revolution, and very generally of a sphere. Within this space a repulsive force exists which preserves it from invasion by other atoms. Outside it, a pressure or force of attraction drives the atoms as close together as possible without causing interpenetration. Chemical combination, therefore, occurs when equilibrium is obtained between atoms of different elements. Attention is drawn to a number of observations illustrating the crystallographic connections between bodies of similar chemical composition. Thus, crystals belonging to the cubic system are characterized by cubical cleavage, when composed of diatomic molecules, as for example, potassium and sodium chlorides, KCl and NaCl. Triatomic molecules, such as calcium fluoride, CaF_2, possess octahedral cleavage.

---

[1] Le Bas, *Proc. Chem. Soc.*, 1907, **23**, 134.

[2] Traube, *Ber.*, 1907, **40**, 734, 723, and 130.

[3] W. J. Sollas, *Proc. Roy. Soc.*, 1898, **63**, 270; 1902, **69**, 294; 1908, **80**, A, 267.

By following along somewhat similar lines to these, Barlow and Pope[1] have been led to suggest a new theory of valency. The atom is conceived of as occupying a definite portion of space, and exerting an influence uniformly in every direction. Since a molecule is usually made up of a number of atoms, it obtains its shape from the way in which the latter are arranged. A crystal is defined as "the homogeneous structure derived by the symmetrical arrangement in space of an indefinitely large number of spheres of atomic influence."

The authors agree with Sollas in assuming that, in an assemblage of atoms, the stability of the molecule is maintained by each atom being subjected to two opposing forces, one of attraction towards the other atoms, and one of repulsion. When these two forces exactly counteract one another, the atoms remain relatively at rest. The repellent force is attributed to the kinetic energy of the atoms, and the attractive force is regarded as akin to gravity.

It will be clear that, if a molecule is so treated, that a portion of it is replaced by another element in such a way that the new assemblage retains the same general arrangement of parts, the total solid volume of the substituting and substituted spheres must be almost the same. For example, by substitution of one atom of chlorine for one of hydrogen in acetic acid, a similar body to the latter is obtained, namely monochloracetic acid. Hence the volume of the sphere of influence of the chlorine atom must be nearly the same as that of the hydrogen atom.

Again, in triphenylamine, $(C_6H_5)_3N$, three atoms of hydrogen have been removed from three molecules of benzene, namely one from each, and their place has been filled by one atom of nitrogen. Hence the volume of the sphere of influence of the nitrogen atom must be very nearly three times that of the hydrogen atom. We thus see that *valency is directly proportional to the volumes of the sphere of atomic influence.* But this proportionality, though close, is not absolutely perfect, for the following reasons :—

---

[1] Barlow and Pope, *Trans. Chem. Soc.*, 1906, **89**, 1675; 1907, **91**, 1150; 1908, **93**, 1528.

1. It appears that the spheres of atomic influence of the various equivalent elements are not quite equal.

2. The volume ratios of the spheres of influence of different elements are somewhat altered by change of condition, as, for example, rise of temperature.

3. The spheres of atomic influence frequently change in magnitude in passing from one compound to another.

From the above it will be clear that the volume occupied by a molecule is approximately the sum of the valencies of the constituent atoms. This is termed the valency volume, W, and involves the assumption that the spheres of atomic influence fill space without interstices. Consider an assemblage of spheres. It will be evident that several single spheres similarly environed, or several groups of two or more spheres, may be removed homogeneously from this assemblage, so as to leave a residual mass of spheres, homogeneous but no longer close-packed. The cavities which have been thus produced may now be filled by a new set of spheres. If the latter possess practically the same volume as those which have been removed, it will clearly be unnecessary to "remarshal" the unremoved spheres, and the new assemblage will have approximately the same configuration as the old. We thus have a theoretical explanation of the Law of Isomorphism discovered empirically by Mitscherlich;[1] for by replacing in a compound an atom of one element by an atom of another belonging to the same group in the Periodic Classification, the resulting compound is isomorphous with the original one. The close connection between isomorphism and valency is, in this way, made apparent.

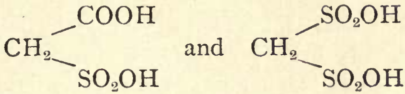
---

[1] Mitscherlich, *Ann. Chim. Phys.*, 1820, **14**, 172; 1821, **19**, 350; 1823, **24**, 264.

It is concluded that, in any vertical column of the Periodic Classification of the elements, the magnitudes of the spheres of atomic influence change but slowly, and in the same direction as the column is descended. The difference between any two adjacent atoms in the same group will therefore be small. In passing from one vertical column to the next, the general magnitude of the spheres changes to such an extent as to amount to a change of valency. The close morphotropic relationships observed by Zirngiebl[1] between benzoic and benzene sulphonic acids, namely

$$C_6H_5.COOH \quad \text{and} \quad C_6H_5.SO_2OH,$$

and between sulpho-acetic and methionic acids,



$$CH_2\begin{cases}COOH\\SO_2OH\end{cases} \quad \text{and} \quad CH_2\begin{cases}SO_2OH\\SO_2OH\end{cases}$$

are particularly interesting, in that they show that a carbon atom of valency volume four, is replaceable by a sulphur and an oxygen atom. Since the valency of the latter is two, we are thus led to the assumption that sulphur in sulphonic acid is essentially divalent.

It is well known that the numerical values of the valencies of those elements which exhibit variable valency usually differ by two, or multiples of two units. Thus gold is mono- and tri-valent. Nitrogen and phosphorus are tri- and penta-valent. Sulphur is di-, tetra-, and hexa-valent. So long as the old ideas prevailed, that the atoms were provided with hooks and eyes, which represented their valencies, a physical interpretation of the above was clear. But the demolition of these crude notions has rendered the explanation of multivalency more difficult.

The suggestion of Barlow and Pope is, to say the least, very ingenious. Imagine an assemblage of close-packed spheres, and let one of these spheres have a valency volume m. If this is removed, and into the cavity thus produced a sphere of volume

---

[1] Zirngiebl, *Zeit. Kryst. Min.*, 1902, **36**, 117.

$m + 1$ is pushed, it will be clear that a second sphere, of valency volume 1, must simultaneously be introduced into the enveloping shell of atoms, if the close-packing is to be restored without remarshalling. This is obviously equivalent to the insertion of an atom of valency 1 in the space already occupied by an atom of valency m, and the filling of the gap thus produced in the enveloping shell by the insertion of a second atom of valency 1. The atom of valency m will thus function as an atom of valency $m + 2$. Similarly, by pushing two atoms of valency 1, or, what comes to the same thing, an atom of valency 2, into the space already filled by an atom of valency m, either two atoms of valency 1, or one of valency 2, must be inserted into the enveloping shell. Consequently the atom originally exhibiting a valency m, now functions as an atom of valency $m + 4$. Sulphur is a case in point.

It has already been pointed out, however, that all atoms exhibiting the same valency have not exactly the same valency volumes. For example, as any vertical column in the Periodic Classification is descended, a slight change in volume is exhibited, although it is not sufficient to change the valency by a whole unit. If, therefore, atoms of valency-volume exactly equal to unity are combined with other atoms of valency-volume intermediate between two whole members, it is clear that various assemblages may be formed, in which the numbers of monovalent atoms attached to one of the polyvalent atoms will not always differ by two. Molybdenum is a good example of this, for the di-, tri-, tetra-, and penta-chlorides, $MoCl_2$, $MoCl_3$, $MoCl_4$, and $MoCl_5$, respectively, are known.

Sufficient has now been said to illustrate the scope of the more important theories which do not regard valency as an electrical phenomenon. There is an unsurmountable objection, however, which can be urged against them all, and that is, the fact that the most stable compounds are formed by the union of elements of opposite electrical character, whereas elements of like electrical character either do not combine at all, or only with difficulty. It would seem, therefore, that the solution of the valency problem is to be sought for in the realm of electricity. There can be little doubt, however, that other forces, such as gravity, etc., exert a disturbing action, and thus tend to greatly complicate the whole subject. But let not the investigator be discouraged. Every new fact, thought, and theory, even though wide of the mark, must ultimately further the interests of science and of truth.

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